G-2876

Work Plan for DNAPL Characterization and Remediation Study

Quality Assurance Project Plan (QAPP)

Sauget Area 1 Sites
Sauget, Illinois

April 1, 2004

GROUNDWATER SERVICES, INC.
Groundwater Services, Inc.
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GROUNDWATER SERVICES, INC.

QUALITY ASSURANCE PROJECT PLAN

Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Revision: 0 Preliminary
April 1, 2004

Prepared for: Solutia Inc.

QA Manager STL Savannah Laboratory	Date
Project Manager STL Savannah Laboratory	Date
QA Manager PTS Geolabs, Inc.	Date
Project Manager PTS Geolabs, Inc.	Date
QA Manager Groundwater Services, Inc.	Date
Project Manager Groundwater Services, Inc.	Date
Project Manager Solutia Inc.	Date
QA Manager USEPA Region 5	Date
Project Coordinator USEPA Region 5	Date

GROUNDWATER SERVICES, INC

TABLE 1
SUMMARY OF SITE I GROUNDWATER CONCENTRATIONS BY DEPTH AND COMPARISON TO CONSTITUENT SOLUBILITY
Sampling Period: November to December 1999

Solutia Inc.
Area 1, Sauget and Cahokia, Illinois

Detected Constituent	0-30 ft Depth Conc. (mg/L)	30-70 ft Depth Conc. (mg/L)	70+ ft Depth Conc. (mg/L)	Solubility (mg/L)
VOCs				
1,1-Dichloroethane	0.96	<0.5	<1.0	5,060
1,1-Dichloroethene	0.032 J	<0.5	<1.0	2,250
Benzene	**0.62**	0.19	0.14 J	1,750
Chlorobenzene	8.7	20.0	**34.0**	***<u>472</u>***
cis/trans-1,2-Dichloroethene	**1.2**	0.31	0.001 J	3,500 (7)
Ethylbenzene	**0.87**	0.27	0.074	169
Tetrachloroethene	<0.5	<0.5	0.001 J	200
Toluene	0.018 J	**0.086 J**	0.00089 J	526
Vinyl Chloride	**0.97**	0.32	0.0012 J	2,760
Xylenes, total	<0.5	0.023 J	0.014	186
SVOCs				
1,2,4-Trichlorobenzene	<0.01	<0.5	**2.7**	300
1,2-Dichlorobenzene	0.13	0.32 J	**0.5**	156
1,3-Dichlorobenzene	0.11	**0.29 J**	0.150 J	NA
1,4-Dichlorobenzene	4.4	**10 D**	9.7 D	***<u>73.8</u>***
2,4,5-Trichlorophenol	<0.01	<0.5	0.0018 J	1,200
2,4-Dichlorophenol	<0.01	0.042	0.047 J	4,500
2-Chlorophenol	0.0055 J	0.039	**0.052**	22,000
2-Methylnaphthalene	<0.01	<0.5	0.0013 J	NA
2-Methylphenol (o-cresol)	<0.01	0.003 J	<0.4	26,000
4-Chloroaniline	**4.1 D**	1.7 D	0.018	5,300
Acenaphthene	<0.01	<0.5	0.00033 J	4.24
Carbazole	0.0014 J	0.013	**0.013**	7.48
Di-n-butylphthalate	<0.01	0.00034 J	0.00051 J	11.2
Dibenzofuran	<0.01	0.019 J	<0.4	NA
Diethylphthalate	<0.01	0.0051 J	<0.4	1,080
Fluoranthene	<0.01	0.022 J	<0.4	***<u>0.206</u>***
Hexachlorobenzene	<0.01	<0.5	0.001 J	6.2
N-Nitrosodiphenylamine	0.0053	**0.028**	0.02	35.1
Naphthalene	0.0042 J	0.024	**0.066**	31
Phenanthrene	<0.01	**0.089 J**	0.0013 J	NA
Phenol	<0.01	0.0044 J	<0.4	82,800
bis(2-chloroethyl)ether	0.0011 J	<0.5	<0.4	17,200
bis(2-ethylhexyl)phthalate	0.00069 J	<0.09	<0.072	0.34
Total Detected Conc. (mg/L)	**22.1**	**33.8**	**47.5**	

Notes:
1) Table includes only those compounds detected in at least one groundwater sample for each constituent class. Comparison to solubility includes groundwater sampled at any depth in source area monitoring well.
2) Groundwater samples included are from nearest source area monitoring well only (i.e., AA-I-S1).
3) J = Estimated value. D = Diluted sample. NA = Not available.
4) **Bold** type denotes maximum groundwater concentration by depth.
5) ***<u>Underlined bold italics</u>*** type denotes maximum groundwater concentration exceeds 1% of constit. solubility.
6) Lowest solubility of cis/trans-1,2-Dichloroethene pair indicated.
7) Solubility data from Illinois Tiered Approach to Corrective Action Objectives (TACO).
8) For comparison purposes, non-detectable concentrations are taken as the detection limit shown.

GROUNDWATER SERVICES, INC.

TABLE 2
SUMMARY OF SITE I GROUNDWATER CONCENTRATIONS BY DEPTH VERSUS TCLP WASTE DATA
Sampling Period: November to December 1999

Solutia Inc.
Area 1, Sauget and Cahokia, Illinois

Detected Constituent	0-30 ft Depth Conc. (mg/L)	30-70 ft Depth Conc. (mg/L)	70+ ft Depth Conc. (mg/L)	Max. TCLP Conc. (mg/L)	Media With Max. Conc.
VOCs					
1,1-Dichloroethane	0.96	<0.5	<1.0	NA	-
1,1-Dichloroethene	**0.032 J**	<0.5	<1.0	<0.02	GW
Benzene	**0.62**	0.19	0.14 J	0.14	GW
Chlorobenzene	8.7	20.0	**34.0**	8.9	GW
cis/trans-1,2-Dichloroethene	1.2	0.31	0.001 J	NA	-
Ethylbenzene	0.87	0.27	0.074	NA	-
Tetrachloroethene	<0.5	<0.5	0.001 J	0.29	-
Toluene	0.018 J	0.086 J	0.00089 J	NA	-
Vinyl Chloride	**0.97**	0.32	0.0012 J	<0.04	GW
Xylenes, total	<0.5	0.023 J	0.014	NA	-
SVOCs					
1,2,4-Trichlorobenzene	<0.01	<0.5	2.7	NA	-
1,2-Dichlorobenzene	0.13	0.32 J	0.5	NA	-
1,3-Dichlorobenzene	0.11	0.29 J	0.150 J	NA	-
1,4-Dichlorobenzene	4.4	**10 D**	9.7 D	1.3	GW
2,4,5-Trichlorophenol	<0.01	<0.5	0.0018 J	**1.4**	TCLP
2,4-Dichlorophenol	<0.01	0.042	0.047 J	NA	-
2-Chlorophenol	0.0055 J	0.039	0.052	NA	-
2-Methylnaphthalene	<0.01	<0.5	0.0013 J	NA	-
2-Methylphenol (o-cresol)	<0.01	0.003 J	<0.4	0.014 J	-
4-Chloroaniline	4.1 D	1.7 D	0.018	NA	-
Acenaphthene	<0.01	<0.5	0.00033 J	NA	-
Carbazole	0.0014 J	0.013	0.013	NA	-
Di-n-butylphthalate	<0.01	0.00034 J	0.00051 J	NA	-
Dibenzofuran	<0.01	0.019 J	<0.4	NA	-
Diethylphthalate	<0.01	0.0051 J	<0.4	NA	-
Fluoranthene	<0.01	0.022 J	<0.4	NA	-
Hexachlorobenzene	<0.01	<0.5	0.001 J	<0.05	-
N-Nitrosodiphenylamine	0.0053	0.028	0.02	NA	-
Naphthalene	0.0042 J	0.024	0.066	NA	-
Phenanthrene	<0.01	0.089 J	0.0013 J	NA	-
Phenol	<0.01	0.0044 J	<0.4	NA	-
bis(2-chloroethyl)ether	0.0011 J	<0.5	<0.4	NA	-
bis(2-ethylhexyl)phthalate	0.00069 J	<0.09	<0.072	NA	-

GW Conc. Greater	5
TCLP Conc. Greater	1

Notes:
1) Table includes only those compounds detected in at least one groundwater sample for each constituent class. Comparison to TCLP waste concentration includes groundwater sampled at any depth in source area monitoring well.
2) Groundwater samples included are collected from nearest source area monitoring well only (i.e., AA-I-S1).
3) J = Estimated value. D = Diluted sample.
4) **Underlined bold** type denotes maximum groundwater concentration or TCLP concentration.
5) TCLP waste data from unsaturated waste samples.
6) NA = Not analyzed.
7) *For comparison purposes, non-detectable concentrations are taken as the detection limit shown.*

GROUNDWATER
SERVICES, INC.

QAPP RECIPIENTS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

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LIST OF ACRONYMNS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

AA	Atomic Absorption
ABN	Acid/Base Neutral Analysis
ACS	American Chemical Society
AOC	Area of Concern
AOI	Area of Investigation
ANPR	Advanced Notice of Proposed Rulemaking
ASTM	American Society of Testing Materials
BFB	Bromofluorobenzene
bgs	Below ground surface
CCC	Calibration Check Compound
CLP	Contract Laboratory Program
CMS	Corrective Measures Study
CRL	Central Regional Laboratory
DDT	Dichlorodiphenyltrichloroethane
DFTPP	Decafluorotriphenylphosphine
DNAPL	Dense Non-Aqueous Phase Liquid
DO	Dissolved Oxygen
DQCR	Daily Quality Control Report
DQO	Data Quality Objective
FCR	Field Change Request
FIP	Facility Investigation Plan
ft	Feet
GC/MS	Gas Chromatograph/Mass Spectrometer
HASP	Health and Safety Plan
HPLC	High Performance Liquid Chromatography
ICP	Inductively Coupled Plasma
IDL	Instrument Detection Limit
lb	Pounds
LCS	Laboratory Control Sample
LIMS	Laboratory Information Management System
LTO	Laboratory Task Order
mg	Milligram
MDL	Method Detection Limit
mL	Milliliter
MS	Matrix Spike
MSD	Matrix Spike Duplicate
MQL	Method Quantitation Limit
NAPL	Non-Aqueous Phase Liquid
ng	Nanogram
NIST	National Institute of Standards and Testing
OEPA	Ohio Environmental Protection Agency
OVA	Organic Vapor Analyzer
PE	Performance Evaluation
PCMT	Potential Corrective Measure Technology

LIST OF ACRONYMNS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

PID	Photoionization Detector
PR/VSI	Preliminary Review/Visual Site Inspection
QAPP	Quality Assurance Project Plan
QA/QC	Quality Assurance/Quality Control
RBC	Risk-Based Concentration
RCRA	Resource Conservation and Recovery Act
RF	Response Factor
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
RT_A	Absolute Retention Time
RWBS	Reagent Water Blank Spike
SOP	Standard Operating Procedure
SOW	Statement of Work
SPCC	System Performance Check Compound
SVOC	Semi-Volatile Organic Compound
SWMU	Solid Waste Management Unit
TCL	Target Compound List
TCLP	Toxicity Characteristic Leaching Procedure
TIC	Tentatively Identified Compound
µg	Microgram
µL	Microliter
USEPA	United States Environmental Protection Agency
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
VTSR	Validated Time of Sample Receipt
WTP	Water Treatment Plant

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1.0 PROJECT DESCRIPTION

1.1 Project Overview

This Quality Assurance Project Plan (QAPP) has been prepared for the Dense Non-Aqueous Phase Liquid (DNAPL) Characterization and Remediation Study to be conducted by Solutia Inc. at the Sauget Area 1 Sites in Sauget, Illinois. The Project Work Plan that accompanies this QAPP describes the project background and investigation objectives, including the site description and history, the project objectives, the sample network design and rationale, and the project schedule. The Field Sampling Program describes procedures to be implemented in the field.

This QAPP describes data quality objectives (DQOs) as well as the field and laboratory procedures to be implemented in order to fulfill the project objectives. This QAPP was prepared in general accordance with applicable U.S. Environmental Protection Agency (EPA) guidance in *Region 5 RCRA Quality Assurance Project Plan Instructions* (USEPA, 1998).

1.2 Objective of the QAPP

The general objective of quality assurance is to collect defensible environmental data of known quality that is adequate for the intended use of the data. To accomplish this objective, data quality objectives (DQOs) have been developed for the DNAPL Study. DQOs are qualitative and quantitative statements which clarify the study objectives, define the most appropriate types of data to collect, determine the most appropriate conditions from which to collect data, and specify acceptable decisions regarding the data's usage (USEPA 1994a). The DQO planning process is a tool to determine which type, quality, and quantity of data will be sufficient to support the subsequent decision-making process. Output from the DQO process is used to develop the sampling plan and select appropriate laboratory analyses. U.S. EPA has identified two broad categories of data (i.e., screening data and definitive data) with corresponding DQO levels, which relate various data uses with the appropriate QA/QC efforts, as well as methods required to achieve a specified level of quality.

Each category has associated with it a set of performance requirements or objectives that enable a comparison to be made between the actual performance of the data collection methods to predetermined performance standards for the analytical parameters. Methods associated with acquisition of screening and definitive data to be collected during the work program are summarized below:

Potential Data Collection Technique	Data Usage
Field	
Drilling and Sampling	Definitive
Measurement of water depths and LNAPL thicknesses	Definitive
Geophysical Survey	Screening
Examination for NAPL Presence	Screening

Potential Data Collection Technique	Data Usage
Laboratory	
Core Properties	Screening
Treatability Tests	Screening
Chemical of Concern Concentrations	Definitive
Soil Properties	Definitive

Screening data to be collected includes the following field activities with respect to soil samples: measurement of organic vapor concentrations and examination for the presence of NAPL. Because the primary use of these data is for relative comparison or for selecting samples to be analyzed by the laboratory, confirmation samples for these parameters will not be analyzed.

Analytical data generated in the laboratory from samples of various site media will be either screening or definitive. Screening data will be obtained from laboratory analysis of soil cores for DNAPL mobility, pore fluid saturation, and fluid properties. American Petroleum Institute (API) or American Society of Testing and Materials (ASTM) methods, as appropriate, will be employed for these analyses. In addition, a series of boiling point curves will be produced by analysis of the pore fluids (NAPL and water) extracted from collected soil cores in order to assess the treatability of the fluids present in the soils beneath the Sauget Area 1 Sites.

Soil, water, and NAPL samples will be analyzed to characterize the concentrations of COCs within these media; consequently, definitive data will be obtained in order to assess the concentration and nature of organic constituents at the site. Analytical parameters for soil, water, and NAPL will include volatile organic compounds (VOCs) and semivolatile organic compounds (SVOCs). Soil will also be analyzed for total organic carbon (TOC) concentration. In addition to VOCs and SVOCs, NAPL will be analyzed for organochlorine pesticides; chlorinated herbicides; polychlorinated biphenyls (PCBs); dioxins and furans; and metals.

Default Tier 1 Remediation Objectives for Industrial/Commercial Properties under the Illinois Tiered Approach to Corrective Action Objectives (TACO) as published in 30 IAC Part 742 represent reasonable targets for analytical precision and have been used to develop project DQOs; however, these values do not necessarily represent appropriate cleanup values for the site. Accordingly, U.S. EPA SW-846 analytical methods have been selected to provide analytical detection limits corresponding to these criteria to the extent feasible. For a limited number of VOCs and SVOCs analyzed by USEPA SW-846 methods, the laboratory reporting limit (RL) is greater than the default Tier 1 TACO value. For these compounds, the project DQO has been set equal to the laboratory RL. DQOs for soil, water, and NAPL samples are summarized in Tables 1.1 through 1.3, respectively. Analytical parameters for soil cores are summarized on Table 1.4

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

TABLES

GROUNDWATER SERVICES, INC.

TABLE 1.1
ANALYTICAL PARAMETERS AND DATA QUALITY OBJECTIVES FOR SOIL
QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep.	Det.	MDL mg/kg	RL mg/kg	Soil Screening Level mg/kg	Investigation DQO (Note 2) mg/kg
Volatile Organics							
Acetone	67-64-1	5035	8260B	8.00E-03	5.00E-02	1.60E+01	1.60E+01
Benzene	71-43-2	5035	8260B	1.10E-03	5.00E-03	3.00E-02	3.00E-02
Bromodichloromethane	75-27-4	5035	8260B	1.30E-03	5.00E-03	6.00E-01	6.00E-01
Bromoform	75-25-2	5035	8260B	1.70E-03	5.00E-03	8.00E-01	8.00E-01
Bromomethane	74-83-9	5035	8260B	3.40E-03	5.00E-03	2.00E-01	2.00E-01
Carbon disulfide	75-15-0	5035	8260B	2.00E-03	5.00E-03	9.00E+00	9.00E+00
Carbon tetrachloride	56-23-5	5035	8260B	9.40E-04	5.00E-03	7.00E-02	7.00E-02
Chlorobenzene	108-90-7	5035	8260B	1.30E-03	5.00E-03	1.00E+00	1.00E+00
Chloroethane	75-00-3	5035	8260B	1.70E-03	5.00E-03	N/A	5.00E-03
Chloroform	67-66-3	5035	8260B	1.20E-03	5.00E-03	5.40E-01	5.40E-01
Chloromethane	74-87-3	5035	8260B	1.40E-03	5.00E-03	N/A	5.00E-03
Dibromochloromethane	124-48-1	5035	8260B	1.40E-03	5.00E-03	4.00E-01	4.00E-01
Dichloroethane, 1,1-	75-34-3	5035	8260B	1.00E-03	5.00E-03	2.30E+01	2.30E+01
Dichloroethane, 1,2-	107-06-2	5035	8260B	1.50E-03	5.00E-03	2.00E-02	2.00E-02
Dichloroethene, 1,1-	75-35-4	5035	8260B	1.70E-03	5.00E-03	6.00E-02	6.00E-02
Dichloroethene, cis-1,2-	156-59-2	5036	8260B	1.10E-03	5.00E-03	4.00E-01	4.00E-01
Dichloroethene, trans-1,2-	156-60-5	5035	8260B	1.20E-03	5.00E-03	7.00E-01	7.00E-01
Dichloropropane, 1,2-	78-87-5	5035	8260B	1.20E-03	5.00E-03	3.00E-02	3.00E-02
Dichloropropene, cis-1,3-	10061-01-5	5035	8260B	1.20E-03	5.00E-03	4.00E-03	5.00E-03
Dichloropropene, trans-1,3-	10061-02-6	5035	8260B	1.60E-03	5.00E-03	4.00E-03	5.00E-03
Ethylbenzene	100-41-4	5035	8260B	1.00E-03	5.00E-03	1.30E+01	1.30E+01
Hexanone, 2-	591-78-6	5035	8260B	5.10E-03	2.50E-02	N/A	2.50E-02
Methyl ethyl ketone (2-Butanone)	78-93-3	5035	8260B	4.70E-03	2.50E-02	N/A	2.50E-02
Methyl-2-pentanone, 4-	108-10-1	5035	8260B	5.00E-03	2.50E-02	N/A	2.50E-02
Methylene chloride	75-09-2	5035	8260B	2.40E-03	5.00E-03	2.00E-02	2.00E-02
Styrene	100-42-5	5035	8260B	1.10E-03	5.00E-03	4.00E+00	4.00E+00
Tetrachloroethane, 1,1,2,2-	79-34-5	5035	8260B	2.00E-03	5.00E-03	N/A	5.00E-03
Tetrachloroethene	127-18-4	5035	8260B	1.50E-03	5.00E-03	6.00E-02	6.00E-02
Toluene	108-88-3	5035	8260B	1.80E-03	5.00E-03	1.20E+01	1.20E+01
Trichloroethane, 1,1,1-	71-55-6	5035	8260B	8.10E-04	5.00E-03	2.00E+00	2.00E+00
Trichloroethane, 1,1,2-	79-00-5	5035	8260B	1.80E-03	5.00E-03	2.00E-02	2.00E-02
Trichloroethene	79-01-6	5035	8260B	1.10E-03	5.00E-03	6.00E-02	6.00E-02
Vinyl chloride	75-01-4	5035	8260B	1.40E-03	5.00E-03	1.00E-02	1.00E-02
Xylenes (total)	1330-20-7	5035	8260B	3.00E-03	1.00E-02	1.50E+02	1.50E+02
Semi-Volatile Organics							
Acenaphthene	83-32-9	3550B	8270C	9.00E-04	6.70E-03	5.70E+02	5.70E+02
Acenaphthylene	208-96-8	3550B	8270C	8.60E-04	6.70E-03	N/A	6.70E-03
Anthracene	120-12-7	3550B	8270C	9.60E-04	6.70E-03	1.20E+04	1.20E+04
Benzo(a)anthracene	56-55-3	3550B	8270C	7.60E-04	6.70E-03	2.00E+00	2.00E+00
Benzo(a)pyrene	50-32-8	3550B	8270C	9.00E-04	6.70E-03	8.00E-01	8.00E-01
Benzo(b)fluoranthene	205-99-2	3550B	8270C	9.60E-04	6.70E-03	5.00E+00	5.00E+00
Benzo(ghi)perylene	191-24-2	3550B	8270C	6.10E-04	6.70E-03	N/A	6.70E-03
Benzo(k)fluoranthene	207-08-9	3550B	8270C	9.80E-04	6.70E-03	4.90E+01	4.90E+01
Bis(2-chloroethoxy) methane	111-91-1	3550B	8270C	3.20E-02	3.30E-01	N/A	3.30E-01
Bis(2-chlorethyl)ether	111-44-4	3550B	8270C	3.70E-02	3.30E-01	4.00E-04	3.30E-01
Bis(2-ethylhexyl) phthalate	117-81-7	3550B	8270C	4.40E-02	3.30E-01	4.10E+02	4.10E+02
Bromophenyl phenyl ether, 4-	101-55-3	3550B	8270C	3.00E-02	3.30E-01	N/A	3.30E-01
Butylbenzyl phthalate	85-68-7	3550B	8270C	3.20E-02	3.30E-01	9.30E+02	9.30E+02
Carbazole	86-74-8	3550B	8270C	3.00E-02	3.30E-01	6.00E-01	6.00E-01
Chloro-3-methylphenol, 4-	59-50-7	3550B	8270C	4.00E-02	3.30E-01	N/A	3.30E-01
Chloroaniline, 4-	106-47-8	3550B	8270C	2.90E-02	6.60E-01	7.00E-01	7.00E-01
Chloronaphthalene, 2-	91-58-7	3550B	8270C	3.70E-02	3.30E-01	N/A	3.30E-01
Chlorophenol, 2-	95-57-8	3550B	8270C	4.10E-02	3.30E-01	4.00E+00	4.00E+00
Chlorophenyl phenyl ether, 4-	7005-72-3	3550B	8270C	2.60E-02	3.30E-01	N/A	3.30E-01
Chrysene	218-01-9	3550B	8270C	1.00E-03	6.70E-03	1.60E+02	1.60E+02
Dibenz(a,h)anthracene	53-70-3	3550B	8270C	8.80E-04	6.70E-03	8.00E-01	8.00E-01
Dibenzofuran	132-64-9	3550B	8270C	3.40E-02	3.30E-01	N/A	3.30E-01
Dichlorobenzene, 1,2-	95-50-1	3550B	8270C	1.10E-03	5.00E-03	1.70E+01	1.70E+01
Dichlorobenzene, 1,3-	541-73-1	3550B	8270C	3.90E-04	5.00E-03	N/A	5.00E-03
Dichlorobenzene, 1,4-	106-46-7	3550B	8270C	5.40E-04	5.00E-03	2.00E+00	2.00E+00

See last page of table for explanatory notes.

GROUNDWATER SERVICES, INC.

TABLE 1.1
ANALYTICAL PARAMETERS AND DATA QUALITY OBJECTIVES FOR SOIL

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep.	Det.	MDL mg/kg	RL mg/kg	Soil Screening Level mg/kg	Investigation DQO (Note 2) mg/kg
Dichlorobenzidine, 3,3'-	91-94-1	3550B	8270C	2.60E-02	6.60E-01	7.00E-03	6.60E-01
Dichlorophenol, 2,4-	120-83-2	3550B	8270C	2.90E-02	3.30E-01	1.00E+00	1.00E+00
Diethylphthalate	84-66-2	3550B	8270C	3.50E-02	3.30E-01	4.70E+02	4.70E+02
Dimethylphenol, 2,4-	105-67-9	3550B	8270C	2.80E-02	3.30E-01	9.00E+00	9.00E+00
Dimethyl phthalate	131-11-3	3550B	8270C	3.50E-02	3.30E-01	N/A	3.30E-01
Di-n-butyl phthalate	84-74-2	3550B	8270C	3.90E-02	3.30E-01	2.30E+03	2.30E+03
Dinitro-o-Cresol, 4,6-	534-52-1	3550B	8270C	3.10E-02	1.70E+00	N/A	1.70E+00
Dinitrophenol, 2,4-	51-28-5	3550B	8270C	3.40E-01	1.70E+00	2.00E-01	1.70E+00
Dinitrotoluene, 2,4-	121-14-2	3550B	8270C	2.20E-02	3.30E-01	8.00E-04	3.30E-01
Dinitrotoluene, 2,6-	606-20-2	3550B	8270C	2.90E-02	3.30E-01	7.00E-04	3.30E-01
Di-n-octyl phthalate	117-84-0	3550B	8270C	3.20E-02	3.30E-01	4.10E+03	4.10E+03
Dinoseb	88-85-7	3550B	8270C	2.70E-02	3.30E-01	3.40E-01	3.40E-01
Fluoranthene	206-44-0	3550B	8270C	8.60E-04	6.70E-03	4.30E+03	4.30E+03
Fluorene	86-73-7	3550B	8270C	7.80E-04	6.70E-03	5.60E+02	5.60E+02
Hexachlorobenzene	118-74-1	3550B	8270C	3.80E-02	3.30E-01	1.80E+00	1.80E+00
Hexachlorobutadiene	87-68-3	3550B	8270C	2.70E-02	3.30E-01	N/A	3.30E-01
Hexachlorocyclopentadiene	77-47-4	3550B	8270C	2.70E-01	3.30E-01	1.10E+00	1.10E+00
Hexachloroethane	67-72-1	3550B	8270C	1.90E-02	3.30E-01	5.00E-01	5.00E-01
Indeno(1,2,3-cd)pyrene	193-39-5	3550B	8270C	6.50E-04	6.70E-03	8.00E+00	8.00E+00
Isophorone	78-59-1	3550B	8270C	2.60E-02	3.30E-01	8.00E+00	8.00E+00
Methylnaphthalene, 2-	91-57-6	3550B	8270C	3.50E-04	6.70E-03	N/A	6.70E-03
Cresol, o-	95-48-7	3550B	8270C	4.60E-02	3.30E-01	1.50E+01	1.50E+01
Cresol, p-	106-44-5	3550B	8270C	4.00E-02	3.30E-01	N/A	3.30E-01
Naphthalene	91-20-3	3550B	8270C	7.10E-04	6.70E-03	1.80E+00	1.80E+00
Nitroaniline, 2-	88-74-4	3550B	8270C	2.50E-02	1.70E+00	N/A	1.70E+00
Nitroaniline, 3-	99-09-2	3550B	8270C	3.00E-02	1.70E+00	N/A	1.70E+00
Nitroaniline, 4-	100-01-6	3550B	8270C	2.60E-02	1.70E+00	N/A	1.70E+00
Nitrobenzene	98-95-3	3550B	8270C	3.10E-02	3.30E-01	1.00E-01	3.30E-01
Nitrophenol, 2-	88-75-5	3550B	8270C	2.60E-02	3.30E-01	N/A	3.30E-01
Nitrophenol, 4-	100-02-7	3550B	8270C	2.50E-02	1.70E+00	N/A	1.70E+00
N-nitrosodi-n-propylamine	621-64-7	3550B	8270C	3.00E-02	3.30E-01	5.00E-05	3.30E-01
Nitrosodiphenylamine, N-	86-30-6	3550B	8270C	3.00E-02	3.30E-01	1.00E+00	1.00E+00
Pentachlorophenol	87-86-5	3550B	8270C	3.40E-02	1.70E+00	3.00E-02	1.70E+00
Phenanthrene	85-01-8	3550B	8270C	8.00E-04	6.70E-03	N/A	6.70E-03
Phenol	108-95-2	3550B	8270C	4.10E-02	3.30E-01	1.00E+02	1.00E+02
Pyrene	129-00-0	3550B	8270C	1.20E-03	6.70E-03	4.20E+03	4.20E+03
Trichlorobenzene, 1,2,4-	120-82-1	3550B	8270C	3.80E-02	3.30E-01	5.00E+00	5.00E+00
Trichlorophenol, 2,4,5-	95-95-4	3550B	8270C	3.10E-02	3.30E-01	2.70E+02	2.70E+02
Trichlorophenol, 2,4,6-	88-06-2	3550B	8270C	3.20E-02	3.30E-01	2.00E-01	3.30E-01
Inorganics							
TOC		NA	EPA-CE Walkely-Black	5.00E+02	5.00E+02	NA	5.00E+02

Notes:
1. Table summarizes proposed analytical methods and data quality objectives (DQOs). Soil screening levels correspond to the lowest Tier 1 soil remediation objective for commercial / industrial (C/I) properties as published in the State of Illinois Tiered Approach to Corrective Action Objectives (TACO) guidelines (35 IAC Part 742). Note that no assumptions regarding the need to clean up to C/I limits are implied here. Tier 1 soil remediation objectives merely represent reasonable target DQOs for soil analyses.
2. Investigation DQOs correspond to the higher of the soil screening level or the reporting limit (RL) for each analyte.
3. Method detection limits (MDLs) and reporting limits (RLs) shown are based on data provided by STL Savannah. Analytical methods are referenced from "Test Methods for Evaluating Solid Wastes, SW-846, Update III, 3rd edition," December 1996.
4. *Physical properties analysis will be performed by PTS Geolabs, Houston, Texas in accordance with ASTM and API standards.*
5. Applicable results will be reported as estimated value between method detection limit (MDL) and the reporting limit (RL).
6. Laboratory MDLs are continuously being evaluated and may differ slightly from these values.
7. Prep. = Digestion or extraction method. — = No value specified.
Det. = Determinative method for quantitation. NA = Not applicable to this constituent.

TABLE 1.2
ANALYTICAL PARAMETERS AND DATA QUALITY OBJECTIVES FOR WATER

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep.	Analytical Method Det.	MDL mg/L	RL mg/L	Screening Level mg/L	Investigation DQO (Note 2) mg/L
Volatile Organics							
Acetone	67-64-1	5030B	8260B	5.00E-03	2.50E-02	7.00E-01	7.00E-01
Benzene	71-43-2	5030B	8260B	3.60E-04	1.00E-03	5.00E-03	5.00E-03
Bromodichloromethane	75-27-4	5030B	8260B	1.40E-04	1.00E-03	2.00E-04	1.00E-03
Bromoform	75-25-2	5030B	8260B	3.30E-04	1.00E-03	1.00E-03	1.00E-03
Bromomethane	74-83-9	5030B	8260B	6.20E-04	1.00E-03	9.80E-03	9.80E-03
Carbon disulfide	75-15-0	5030B	8260B	6.60E-04	1.00E-03	7.00E-01	7.00E-01
Carbon tetrachloride	56-23-5	5030B	8260B	3.10E-04	1.00E-03	5.00E-03	5.00E-03
Chlorobenzene	108-90-7	5030B	8260B	3.40E-04	1.00E-03	1.00E-01	1.00E-01
Chloroethane	75-00-3	5030B	8260B	7.80E-04	1.00E-03	N/A	1.00E-03
Chloroform	67-66-3	5030B	8260B	3.70E-04	1.00E-03	2.00E-04	1.00E-03
Chloromethane	74-87-3	5030B	8260B	3.90E-04	1.00E-03	N/A	1.00E-03
Dibromochloromethane	124-48-1	5030B	8260B	5.00E-04	1.00E-03	1.40E-01	1.40E-01
Dichloroethane, 1,1-	75-34-3	5030B	8260B	3.60E-04	1.00E-03	7.00E-01	7.00E-01
Dichloroethane, 1,2-	107-06-2	5030B	8260B	2.60E-04	1.00E-03	5.00E-03	5.00E-03
Dichloroethene, 1,1-	75-35-4	5030B	8260B	3.60E-04	1.00E-03	7.00E-03	7.00E-03
Dichloroethene, cis-1,2-	156-59-2	5030B	8260B	3.80E-04	1.00E-03	7.00E-02	7.00E-02
Dichloroethene, trans-1,2-	156-60-5	5030B	8260B	4.00E-04	1.00E-03	1.00E-01	1.00E-01
Dichloropropane, 1,2-	78-87-5	5030B	8260B	3.30E-04	1.00E-03	5.00E-03	5.00E-03
Dichloropropene, cis-1,3-	10061-01-5	5030B	8260B	2.30E-04	1.00E-03	N/A	1.00E-03
Dichloropropene, trans-1,3-	10061-02-6	5030B	8260B	2.60E-04	1.00E-03	N/A	1.00E-03
Ethylbenzene	100-41-4	5030B	8260B	3.40E-04	1.00E-03	7.00E-01	7.00E-01
Hexanone, 2-	591-78-6	5030B	8260B	9.30E-04	1.00E-02	N/A	1.00E-02
Methyl Ethyl Ketone (Butanone, -2)	78-93-3	5030B	8260B	1.30E-03	1.00E-02	N/A	1.00E-02
Methyl-2-pentanone, 4-	108-10-1	5030B	8260B	6.50E-04	1.00E-02	N/A	1.00E-02
Methylene chloride	75-09-2	5030B	8260B	6.40E-04	5.00E-03	5.00E-03	5.00E-03
Styrene	100-42-5	5030B	8260B	2.50E-04	1.00E-03	1.00E-01	1.00E-01
Tetrachloroethane, 1,1,2,2-	79-34-5	5030B	8260B	1.80E-04	1.00E-03	N/A	1.00E-03
Tetrachloroethene	127-18-4	5030B	8260B	3.50E-04	1.00E-03	5.00E-03	5.00E-03
Toluene	108-88-3	5030B	8260B	5.40E-04	1.00E-03	1.00E+00	1.00E+00
Trichloroethane, 1,1,1-	71-55-6	5030B	8260B	3.20E-04	1.00E-03	2.00E-01	2.00E-01
Trichloroethane, 1,1,2-	79-00-5	5030B	8260B	2.20E-04	1.00E-03	5.00E-03	5.00E-03
Trichloroethene	79-01-6	5030B	8260B	3.70E-04	1.00E-03	5.00E-03	5.00E-03
Vinyl chloride	75-01-4	5030B	8260B	5.60E-04	1.00E-03	2.00E-03	2.00E-03
Xylenes (total)	1330-20-7	5030B	8260B	1.30E-03	2.00E-03	1.00E+01	1.00E+01
Semi-Volatile Organics							
Acenaphthene	83-32-9	3510C/3520C	8270C	2.50E-05	2.00E-04	4.20E-01	4.20E-01
Acenaphthylene	208-96-8	3510C/3520C	8270C	2.40E-05	2.00E-04	N/A	2.00E-04
Anthracene	120-12-7	3510C/3520C	8270C	3.10E-05	2.00E-04	2.10E+00	2.10E+00
Benzo(a)anthracene	56-55-3	3510C/3520C	8270C	7.00E-05	2.00E-04	1.30E-04	2.00E-04
Benzo(a)pyrene	50-32-8	3510C/3520C	8270C	6.00E-05	2.00E-04	2.00E-04	2.00E-04
Benzo(b)fluoranthene	205-99-2	3510C/3520C	8270C	7.40E-05	2.00E-04	1.80E-04	2.00E-04
Benzo(ghi)perylene	191-24-2	3510C/3520C	8270C	9.60E-05	2.00E-04	N/A	2.00E-04
Benzo(k)fluoranthene	207-08-9	3510C/3520C	8270C	5.80E-05	2.00E-04	1.70E-04	2.00E-04
Bis(2-chloroethoxy) methane	111-91-1	3510C/3520C	8270C	1.00E-03	1.00E-02	N/A	1.00E-02
Bis(2-chlorethyl)ether	111-44-4	3510C/3520C	8270C	1.00E-03	1.00E-02	1.00E-02	1.00E-02
Bis(2-ethylhexyl) phthalate	117-81-7	3510C/3520C	8270C	2.40E-03	1.00E-02	6.00E-03	1.00E-02
Bromophenyl phenyl ether, 4-	101-55-3	3510C/3520C	8270C	1.00E-03	1.00E-02	N/A	1.00E-02
Butylbenzyl phthalate	85-68-7	3510C/3520C	8270C	7.40E-04	1.00E-02	1.40E+00	1.40E+00
Carbazole	86-74-8	3510C/3520C	8270C	5.40E-04	1.00E-02	N/A	1.00E-02
Chloro-3-methylphenol, 4-	59-50-7	3510C/3520C	8270C	1.00E-03	1.00E-02	N/A	1.00E-02
Chloroaniline, 4-	106-47-8	3510C/3520C	8270C	1.00E-03	2.00E-02	2.80E-02	2.80E-02
Chloronaphthalene, 2-	91-58-7	3510C/3520C	8270C	1.00E-03	1.00E-02	N/A	1.00E-02
Chlorophenol, 2-	95-57-8	3510C/3520C	8270C	7.90E-04	1.00E-02	3.50E-02	3.50E-02
Chlorophenyl phenyl ether, 4-	7005-72-3	3510C/3520C	8270C	7.00E-04	1.00E-02	N/A	1.00E-02
Chrysene	218-01-9	3510C/3520C	8270C	8.80E-05	2.00E-04	1.50E-03	1.50E-03
Dibenz(a,h)anthracene	53-70-3	3510C/3520C	8270C	6.50E-05	2.00E-04	3.00E-04	3.00E-04
Dibenzofuran	132-64-9	3510C/3520C	8270C	1.00E-03	1.00E-02	N/A	1.00E-02
Dichlorobenzene, 1,2-	95-50-1	3510C/3520C	8270C	2.10E-04	1.00E-03	6.00E-01	6.00E-01
Dichlorobenzene, 1,3-	541-73-1	3510C/3520C	8270C	1.20E-04	1.00E-03	N/A	1.00E-03
Dichlorobenzene, 1,4-	106-46-7	3510C/3520C	8270C	1.10E-04	1.00E-03	7.50E-02	7.50E-02

See last page of table for explanatory notes.

TABLE 1.2
ANALYTICAL PARAMETERS AND DATA QUALITY OBJECTIVES FOR WATER

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method		MDL	RL	Screening Level	Investigation DQO (Note 2)
		Prep.	Det.	mg/L	mg/L	mg/L	mg/L
Dichlorobenzidine, 3,3'-	91-94-1	3510C/3520C	8270C	1.00E-03	2.00E-02	2.00E-02	2.00E-02
Dichlorophenol, 2,4-	120-83-2	3510C/3520C	8270C	7.60E-04	1.00E-02	2.10E-02	2.10E-02
Diethylphthalate	84-66-2	3510C/3520C	8270C	1.00E-03	1.00E-02	5.60E+00	5.60E+00
Dimethylphenol, 2,4-	105-67-9	3510C/3520C	8270C	1.10E-03	1.00E-02	1.40E-01	1.40E-01
Dimethyl phthalate	131-11-3	3510C/3520C	8270C	5.70E-04	1.00E-02	N/A	1.00E-02
Di-n-butyl phthalate	84-74-2	3510C/3520C	8270C	1.00E-03	1.00E-02	7.00E-01	7.00E-01
Dinitro-o-Cresol, 4,6-	534-52-1	3510C/3520C	8270C	1.00E-02	5.00E-02	N/A	5.00E-02
Dinitrophenol, 2,4-	51-28-5	3510C/3520C	8270C	1.00E-02	5.00E-02	1.40E-02	5.00E-02
Dinitrotoluene, 2,4-	121-14-2	3510C/3520C	8270C	1.10E-03	1.00E-02	2.00E-05	1.00E-02
Dinitrotoluene, 2,6-	606-20-2	3510C/3520C	8270C	8.70E-04	1.00E-02	3.10E-04	1.00E-02
Di-n-octyl phthalate	117-84-0	3510C/3520C	8270C	1.20E-03	1.00E-02	1.40E-01	1.40E-01
Dinoseb	88-85-7	3510C/3520C	8270C	7.80E-01	1.00E-02	7.00E-03	1.00E-02
Fluoranthene	206-44-0	3510C/3520C	8270C	6.10E-05	2.00E-04	2.80E-01	2.80E-01
Fluorene	86-73-7	3510C/3520C	8270C	2.60E-05	2.00E-04	2.80E-01	2.80E-01
Hexachlorobenzene	118-74-1	3510C/3520C	8270C	6.10E-04	1.00E-02	6.00E-05	1.00E-02
Hexachlorobutadiene	87-68-3	3510C/3520C	8270C	5.00E-04	1.00E-02	N/A	1.00E-02
Hexachlorocyclopentadiene	77-47-4	3510C/3520C	8270C	1.10E-03	1.00E-02	5.00E-02	5.00E-02
Hexachloroethane	67-72-1	3510C/3520C	8270C	7.00E-04	1.00E-02	7.00E-03	1.00E-02
Indeno(1,2,3-cd)pyrene	193-39-5	3510C/3520C	8270C	8.00E-05	2.00E-04	4.30E-04	4.30E-04
Isophorone	78-59-1	3510C/3520C	8270C	1.00E-03	1.00E-02	1.40E+00	1.40E+00
Methylnaphthalene, 2-	91-57-6	3510C/3520C	8270C	2.20E-05	2.00E-04	N/A	2.00E-04
Cresol, o-	95-48-7	3510C/3520C	8270C	5.90E-04	1.00E-02	3.50E-01	3.50E-01
Cresol, p-	106-44-5	3510C/3520C	8270C	1.00E-03	1.00E-02	N/A	1.00E-02
Naphthalene	91-20-3	3510C/3520C	8270C	2.80E-05	2.00E-04	1.40E-01	1.40E-01
Nitroaniline, 2-	88-74-4	3510C/3520C	8270C	7.20E-04	5.00E-02	N/A	5.00E-02
Nitroaniline, 3-	99-09-2	3510C/3520C	8270C	6.40E-04	5.00E-02	N/A	5.00E-02
Nitroaniline, 4-	100-01-6	3510C/3520C	8270C	8.60E-04	5.00E-02	N/A	5.00E-02
Nitrobenzene	98-95-3	3510C/3520C	8270C	1.00E-03	1.00E-02	3.50E-03	1.00E-02
Nitrophenol, 2-	88-75-5	3510C/3520C	8270C	1.10E-03	1.00E-02	N/A	1.00E-02
Nitrophenol, 4-	100-02-7	3510C/3520C	8270C	5.00E-03	5.00E-02	N/A	5.00E-02
N-nitrosodi-n-propylamine	621-64-7	3510C/3520C	8270C	1.00E-03	1.00E-02	1.80E-03	1.00E-02
Nitrosodiphenylamine, N-	86-30-6	3510C/3520C	8270C	1.00E-03	1.00E-02	3.20E-03	1.00E-02
Pentachlorophenol	87-86-5	3510C/3520C	8270C	2.00E-03	5.00E-02	1.00E-03	5.00E-02
Phenanthrene	85-01-8	3510C/3520C	8270C	2.50E-05	2.00E-04	N/A	2.00E-04
Phenol	108-95-2	3510C/3520C	8270C	1.00E-03	1.00E-02	1.00E-01	1.00E-01
Pyrene	129-00-0	3510C/3520C	8270C	4.20E-05	2.00E-04	2.10E-01	2.10E-01
Trichlorobenzene, 1,2,4-	120-82-1	3510C/3520C	8270C	5.10E-04	1.00E-02	7.00E-02	7.00E-02
Trichlorophenol, 2,4,5-	95-95-4	3510C/3520C	8270C	1.10E-03	1.00E-02	7.00E-01	7.00E-01
Trichlorophenol, 2,4,6-	88-06-2	3510C/3520C	8270C	1.10E-03	1.00E-02	1.00E-02	1.00E-02

Notes:
1. *Table summarizes proposed analytical methods and data quality objectives (DQOs). Water screening levels correspond to the lowest Tier 1 water remediation objective for commercial / industrial (C/I) properties as published in the State of Illinois Tiered Approach to Corrective Action Objectives (TACO) guidelines (35 IAC Part 742). Note that no assumptions regarding the need to clean up to C/I limits are implied here. Tier 1 soil remediation objectives merely represent reasonable target DQOs for soil analyses.*
2. Investigation DQOs correspond to the higher of the water screening level or the reporting limit (RL) for each analyte.
3. *Method detection limits (MDLs) and reporting limits (RLs) shown are based on data provided by STL Savannah. Analytical methods are referenced from "Test Methods for Evaluating Solid Wastes, SW-846, Update III, 3rd edition," December 1996.*
4. Applicable results will be reported as estimated value between method detection limit (MDL) and the reporting limit (RL).
5. Laboratory MDLs are continuously being evaluated and may differ slightly from these values.
6. Prep. = Digestion or extraction method.
   Det. = Determinative method for quantitation.

— = No value specified.
NA = Not applicable to this constituent.

GROUNDWATER SERVICES, INC.

TABLE 1.3
ANALYTICAL PARAMETERS AND DATA QUALITY OBJECTIVES FOR NAPL

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep.	Det.	MDL mg/Kg	RL mg/Kg	Investigation DQO (Note 2) mg/kg
Volatile Organics						
Acetone	67-64-1	3585	8260B	5.10E+03	2.00E+04	2.00E+04
Benzene	71-43-2	3585	8260B	4.60E+02	2.00E+03	2.00E+03
Bromodichloromethane	75-27-4	3585	8260B	8.60E+02	2.00E+03	2.00E+03
Bromoform	75-25-2	3585	8260B	4.50E+02	2.00E+03	2.00E+03
Bromomethane	74-83-9	3585	8260B	1.00E+03	2.00E+03	2.00E+03
Carbon disulfide	75-15-0	3585	8260B	7.80E+02	2.00E+03	2.00E+03
Carbon tetrachloride	56-23-5	3585	8260B	1.20E+03	2.00E+03	2.00E+03
Chlorobenzene	108-90-7	3585	8260B	6.20E+02	2.00E+03	2.00E+03
Chloroethane	75-00-3	3585	8260B	1.00E+03	2.00E+03	2.00E+03
Chloroform	67-66-3	3585	8260B	3.90E+02	2.00E+03	2.00E+03
Chloromethane	74-87-3	3585	8260B	1.00E+03	2.00E+03	2.00E+03
Dibromochloromethane	124-48-1	3585	8260B	6.60E+02	2.00E+03	2.00E+03
Dichloroethane, 1,1-	75-34-3	3585	8260B	3.50E+02	2.00E+03	2.00E+03
Dichloroethane, 1,2-	107-06-2	3585	8260B	1.00E+03	2.00E+03	2.00E+03
Dichloroethene, 1,1-	75-35-4	3585	8260B	8.20E+02	2.00E+03	2.00E+03
Dichloroethene, cis-1,2-	156-59-2	3585	8260B	5.80E+02	2.00E+03	2.00E+03
Dichloroethene, trans-1,2-	156-60-5	3585	8260B	5.20E+02	2.00E+03	2.00E+03
Dichloropropane, 1,2-	78-87-5	3585	8260B	9.60E+02	2.00E+03	2.00E+03
Dichloropropene, cis-1,3-	10061-01-5	3585	8260B	1.00E+03	2.00E+03	2.00E+03
Dichloropropene, trans-1,3-	10061-02-6	3585	8260B	5.90E+02	2.00E+03	2.00E+03
Ethylbenzene	100-41-4	3585	8260B	5.00E+02	2.00E+03	2.00E+03
Hexanone, 2-	591-78-6	3585	8260B	5.00E+03	1.00E+04	1.00E+04
Methyl ethyl ketone (2-Butanone)	78-93-3	3585	8260B	1.70E+03	1.00E+04	1.00E+04
Methyl-2-pentanone, 4-	108-10-1	3585	8260B	1.40E+03	1.00E+04	1.00E+04
Methylene chloride	75-09-2	3585	8260B	5.10E+02	2.00E+03	2.00E+03
Styrene	100-42-5	3585	8260B	1.30E+03	2.00E+03	2.00E+03
Tetrachloroethane, 1,1,2,2-	79-34-5	3585	8260B	7.90E+02	2.00E+03	2.00E+03
Tetrachloroethene	127-18-4	3585	8260B	8.90E+02	2.00E+03	2.00E+03
Toluene	108-88-3	3585	8260B	6.30E+02	2.00E+03	2.00E+03
Trichloroethane, 1,1,1-	71-55-6	3585	8260B	1.10E+03	2.00E+03	2.00E+03
Trichloroethane, 1,1,2-	79-00-5	3585	8260B	4.10E+02	2.00E+03	2.00E+03
Trichloroethene	79-01-6	3585	8260B	1.00E+03	2.00E+03	2.00E+03
Vinyl chloride	75-01-4	3585	8260B	1.00E+03	2.00E+03	2.00E+03
Xylenes (total)	1330-20-7	3585	8260B	1.40E+03	4.00E+03	4.00E+03
Semi-Volatile Organics						
Acenaphthene	83-32-9	3580	8270C	1.00E+04	1.00E+05	1.00E+05
Acenaphthylene	208-96-8	3580	8270C	7.50E+03	1.00E+05	1.00E+05
Anthracene	120-12-7	3580	8270C	9.60E+03	1.00E+05	1.00E+05
Benzo(a)anthracene	56-55-3	3580	8270C	1.08E+04	1.00E+05	1.00E+05
Benzo(a)pyrene	50-32-8	3580	8270C	9.60E+03	1.00E+05	1.00E+05
Benzo(b)fluoranthene	205-99-2	3580	8270C	9.90E+03	1.00E+05	1.00E+05
Benzo(ghi)perylene	191-24-2	3580	8270C	6.90E+03	1.00E+05	1.00E+05
Benzo(k)fluoranthene	207-08-9	3580	8270C	3.90E+03	1.00E+05	1.00E+05
Bis(2-chloroethoxy) methane	111-91-1	3580	8270C	3.90E+03	1.00E+05	1.00E+05
Bis(2-chlorethyl)ether	111-44-4	3580	8270C	1.10E+04	1.00E+05	1.00E+05
Bis(2-ethylhexyl) phthalate	117-81-7	3580	8270C	1.30E+04	1.00E+05	1.00E+05
Bromophenyl phenyl ether, 4-	101-55-3	3580	8270C	9.00E+03	1.00E+05	1.00E+05
Butylbenzyl phthalate	85-68-7	3580	8270C	9.60E+03	1.00E+05	1.00E+05
Carbazole	86-74-8	3580	8270C	NA	NA	NA
Chloro-3-methylphenol, 4-	59-50-7	3580	8270C	1.20E+04	1.00E+05	1.00E+05
Chloroaniline, 4-	106-47-8	3580	8270C	8.70E+03	2.00E+05	2.00E+05
Chloronaphthalene, 2-	91-58-7	3580	8270C	1.10E+04	1.00E+05	1.00E+05
Chlorophenol, 2-	95-57-8	3580	8270C	1.20E+04	1.00E+05	1.00E+05
Chlorophenyl phenyl ether, 4-	7005-72-3	3580	8270C	7.80E+03	1.00E+05	1.00E+05
Chrysene	218-01-9	3580	8270C	9.30E+03	1.00E+05	1.00E+05
Dibenz(a,h)anthracene	53-70-3	3580	8270C	9.30E+03	1.00E+05	1.00E+05
Dibenzofuran	132-64-9	3580	8270C	1.00E+04	1.00E+05	1.00E+05
Dichlorobenzene, 1,2-	95-50-1	3580	8270C	6.90E+03	1.00E+05	1.00E+05
Dichlorobenzene, 1,3-	541-73-1	3580	8270C	6.90E+03	1.00E+05	1.00E+05
Dichlorobenzene, 1,4-	106-46-7	3580	8270C	7.20E+03	1.00E+05	1.00E+05

See last page of table for explanatory notes.

TABLE 1.3
ANALYTICAL PARAMETERS AND DATA QUALITY OBJECTIVES FOR NAPL
QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep.	Det.	MDL mg/Kg	RL mg/Kg	Investigation DQO (Note 2) mg/kg
Dichlorobenzidine, 3,3'-	91-94-1	3580	8270C	7.80E+03	2.00E+05	2.00E+05
Dichlorophenol, 2,4-	120-83-2	3580	8270C	8.70E+03	1.00E+05	1.00E+05
Diethylphthalate	84-66-2	3580	8270C	1.00E+04	1.00E+05	1.00E+05
Dimethylphenol, 2,4-	105-67-9	3580	8270C	8.40E+03	1.00E+05	1.00E+05
Dimethyl phthalate	131-11-3	3580	8270C	1.00E+04	1.00E+05	1.00E+05
Di-n-butyl phthalate	84-74-2	3580	8270C	1.20E+04	1.00E+05	1.00E+05
Dinitro-o-Cresol, 4,6-	534-52-1	3580	8270C	9.30E+03	5.00E+05	5.00E+05
Dinitrophenol, 2,4-	51-28-5	3580	8270C	1.00E+05	5.00E+05	5.00E+05
Dinitrotoluene, 2,4-	121-14-2	3580	8270C	6.60E+03	1.00E+05	1.00E+05
Dinitrotoluene, 2,6-	606-20-2	3580	8270C	8.70E+03	1.00E+05	1.00E+05
Di-n-octyl phthalate	117-84-0	3580	8270C	9.60E+03	1.00E+05	1.00E+05
Dinoseb	88-85-7	3580	8270C	NA	NA	1.00E+05
Fluoranthene	206-44-0	3580	8270C	9.00E+03	1.00E+05	1.00E+05
Fluorene	86-73-7	3580	8270C	6.60E+03	1.00E+05	1.00E+05
Hexachlorobenzene	118-74-1	3580	8270C	1.10E+04	1.00E+05	1.00E+05
Hexachlorobutadiene	87-68-3	3580	8270C	8.10E+03	1.00E+05	1.00E+05
Hexachlorocyclopentadiene	77-47-4	3580	8270C	8.10E+04	1.00E+05	#REF!
Hexachloroethane	67-72-1	3580	8270C	5.70E+03	1.00E+05	1.00E+05
Indeno(1,2,3-cd)pyrene	193-39-5	3580	8270C	5.10E+03	1.00E+05	1.00E+05
Isophorone	78-59-1	3580	8270C	7.80E+03	1.00E+05	1.00E+05
Methylnaphthalene, 2-	91-57-6	3580	8270C	8.70E+03	1.00E+05	1.00E+05
Cresol, o-	95-48-7	3580	8270C	1.40E+04	1.00E+05	1.00E+05
Cresol, p-	106-44-5	3580	8270C	1.20E+04	1.00E+05	1.00E+05
Naphthalene	91-20-3	3580	8270C	9.30E+03	1.00E+05	1.00E+05
Nitroaniline, 2-	88-74-4	3580	8270C	7.50E+03	5.00E+05	5.00E+05
Nitroaniline, 3-	99-09-2	3580	8270C	9.00E+03	5.00E+05	5.00E+05
Nitroaniline, 4-	100-01-6	3580	8270C	7.80E+03	5.00E+05	5.00E+05
Nitrobenzene	98-95-3	3580	8270C	9.30E+03	1.00E+05	1.00E+05
Nitrophenol, 2-	88-75-5	3580	8270C	7.80E+03	1.00E+05	1.00E+05
Nitrophenol, 4-	100-02-7	3580	8270C	7.50E+03	5.00E+05	5.00E+05
N-nitrosodi-n-propylamine	621-64-7	3580	8270C	9.00E+03	1.00E+05	1.00E+05
Nitrosodiphenylamine, N-	86-30-6	3580	8270C	9.00E+03	1.00E+05	1.00E+05
Pentachlorophenol	87-86-5	3580	8270C	1.00E+04	5.00E+05	5.00E+05
Phenanthrene	85-01-8	3580	8270C	1.00E+04	1.00E+05	1.00E+05
Phenol	108-95-2	3580	8270C	1.20E+04	1.00E+05	1.00E+05
Pyrene	129-00-0	3580	8270C	4.50E+03	1.00E+05	1.00E+05
Trichlorobenzene, 1,2,4-	120-82-1	3580	8270C	1.10E+04	1.00E+05	1.00E+05
Trichlorophenol, 2,4,5-	95-95-4	3580	8270C	9.30E+03	1.00E+05	1.00E+05
Trichlorophenol, 2,4,6-	88-06-2	3580	8270C	9.60E+03	1.00E+05	1.00E+05
Metals						
Aluminum	7429-90-5	3050B	6010B	1.40E+00	2.00E+01	2.00E+01
Antimony	7440-36-0	3050B	6010B	6.60E-01	2.00E+00	2.00E+00
Arsenic	7440-38-2	3050B	6010B	7.40E-01	1.00E+00	1.00E+00
Barium	7440-39-3	3050B	6010B	1.00E-01	1.00E+00	1.00E+00
Beryllium	7440-41-7	3050B	6010B	4.00E-02	4.00E-01	4.00E-01
Cadmium	7440-43-9	3050B	6010B	5.60E-02	5.00E-01	5.00E-01
Calcium	7440-70-2	3050B	6010B	5.00E+00	5.00E+01	5.00E+01
Chromium	7440-47-3	3050B	6010B	1.10E-01	1.00E+00	1.00E+00
Cobalt	7440-48-4	3050B	6010B	1.60E-01	1.00E+00	1.00E+00
Copper	7440-50-8	3050B	6010B	2.00E-01	2.00E+00	2.00E+00
Iron	7439-89-6	3050B	6010B	1.60E+00	5.00E+00	5.00E+00
Lead	7439-92-1	3050B	6010B	3.40E-01	5.00E-01	5.00E-01
Magnesium	7439-95-4	3050B	6010B	5.00E+00	5.00E+01	5.00E+01
Mercury	7439-97-6	NA	7471A	1.00E-01	1.00E+00	1.00E+00
Nickel	7440-02-0	3050B	6010B	2.40E-01	4.00E+00	4.00E+00
Potassium	7440-09-7	3050B	6010B	1.00E+01	1.00E+02	1.00E+02
Selenium	7782-49-2	3050B	6010B	7.80E-01	1.00E+00	1.00E+00
Silver	7440-22-4	3050B	6010B	1.20E-01	1.00E+00	1.00E+00
Sodium	7440-23-5	3050B	6010B	1.70E+01	5.00E+01	5.00E+01
Thallium	7440-28-0	3050B	6010B	9.30E-01	1.00E+00	1.00E+00
Vanadium	7440-62-2	3050B	6010B	1.20E-01	1.00E+00	1.00E+00
Zinc	7440-66-6	3050B	6010B	1.30E-01	2.00E+00	2.00E+00

See last page of table for explanatory notes.

GROUNDWATER SERVICES, INC.

TABLE 1.3
ANALYTICAL PARAMETERS AND DATA QUALITY OBJECTIVES FOR NAPL

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep.	Det.	MDL mg/Kg	RL mg/Kg	Investigation DQO (Note 2) mg/kg
Pesticides						
Aldrin	309-00-2	3580	8081	3.30E+00	5.00E+01	5.00E+01
alpha-BHC	319-84-6	3580	8081	7.20E+00	5.00E+01	5.00E+01
beta-BHC	319-85-7	3580	8081	8.70E+00	5.00E+01	5.00E+01
Gamma-BHC (Lindane)	58-89-9	3580	8081	4.50E+00	5.00E+01	5.00E+01
delta-BHC	319-86-8	3580	8081	3.60E+00	5.00E+01	5.00E+01
alpha Chlordane	5103-71-9	3580	8081	3.30E+00	5.00E+01	5.00E+01
Gamma Chlordane	5103-74-2	3580	8081	3.90E+00	5.00E+01	5.00E+01
4,4'-DDD	72-54-8	3580	8081	1.05E+01	1.00E+02	1.00E+02
4,4'-DDE	72-55-9	3580	8081	1.62E+01	1.00E+02	1.00E+02
4,4'-DDT	50-29-3	3580	8081	9.30E+00	1.00E+02	1.00E+02
Dieldrin	60-57-1	3580	8081	9.30E+00	1.00E+02	1.00E+02
Endosulfan I	959-98-8	3580	8081	5.10E+00	5.00E+01	5.00E+01
Endosulfan II	33213-65-9	3580	8081	6.60E+00	1.00E+02	1.00E+02
Endosulfan sulfate	1031-07-8	3580	8081	1.32E+01	1.00E+02	1.00E+02
Endrin	72-20-8	3580	8081	1.29E+01	1.00E+02	1.00E+02
Endrin aldehyde	7421-93-4	3580	8081	9.30E+00	1.00E+02	1.00E+02
Endrin ketone	53494-70-5	3580	8081	1.14E+01	1.00E+02	1.00E+02
Heptachlor	76-44-8	3580	8081	8.40E+00	5.00E+01	5.00E+01
Heptachlor epoxide	1024-57-3	3580	8081	5.10E+00	5.00E+01	5.00E+01
Methoxychlor	72-43-5	3580	8081	6.00E+00	5.00E+02	5.00E+02
Toxaphene	8001-35-2	3580	8081	9.90E+02	5.00E+03	5.00E+03
Herbicides						
2,4-D	94-75-7	3580	8151	NA	NA	NA
Dalapon	75-99-0	3580	8151	NA	NA	NA
2,4-DB	94-82-6	3580	8151	NA	NA	NA
Dicamba	1918-00-9	3580	8151	NA	NA	NA
Dichloroprop	120-36-5	3580	8151	NA	NA	NA
MCPA	94-74-6	3580	8151	NA	NA	NA
MCPP	7085-19-0/ 93-65-2	3580	8151	NA	NA	NA
Pentachlorophenol	87-86-5	3580	8151	NA	NA	NA
2,4,5-T	93-76-5	3580	8151	NA	NA	NA
2,4,5-TP (Silvex)	93-72-1	3580	8151	NA	NA	NA
PCBs						
Aroclor 1016	NA	3580	8082	1.20E+02	1.00E+03	1.00E+03
Aroclor 1221	NA	3580	8082	5.10E+02	2.00E+03	2.00E+03
Aroclor 1232	NA	3580	8082	2.00E+02	1.00E+03	1.00E+03
Aroclor 1242	NA	3580	8082	2.00E+02	1.00E+03	1.00E+03
Aroclor 1248	NA	3580	8082	2.00E+02	1.00E+03	1.00E+03
Aroclor 1254	NA	3580	8082	2.00E+02	1.00E+03	1.00E+03
Aroclor 1260	NA	3580	8082	1.30E+02	1.00E+03	1.00E+03

See last page of table for explanatory notes.

GROUNDWATER SERVICES, INC.

TABLE 1.3
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QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep.	Det.	PQL ng/g	DQL mg/Kg	Investigation DQO (Note 2) mg/kg
Dioxins and Furans						
2,3,7,8-TCDD	1746-01-6	NA	8280A	NA	NA	NA
1,2,3,7,8-PeCDD	40321-76-4	NA	8280A	NA	NA	NA
1,2,3,4,7,8-HxCDD	39227-28-6	NA	8280A	NA	NA	NA
1,2,3,6,7,8-HxCDD	57653-85-7	NA	8280A	NA	NA	NA
1,2,3,7,8,9-HxCDD	19408-74-3	NA	8280A	NA	NA	NA
1,2,3,4,6,7,8-HpCDD	35822-39-4	NA	8280A	NA	NA	NA
OCDD	3268-87-9	NA	8280A	NA	NA	NA
2,3,7,8-TCDF	51207-31-9	NA	8280A	NA	NA	NA
1,2,3,7,8-PeCDF	57117-41-6	NA	8280A	NA	NA	NA
2,3,4,7,8-PeCDF	57117-31-4	NA	8280A	NA	NA	NA
1,2,3,4,7,8-HxCDF	70648-26-9	NA	8280A	NA	NA	NA
1,2,3,6,7,8-HxCDF	57117-44-9	NA	8280A	NA	NA	NA
2,3,4,6,7,8-HxCDF	60851-34-5	NA	8280A	NA	NA	NA
1,2,3,7,8,9-HxCDF	72918-21-9	NA	8280A	NA	NA	NA
1,2,3,4,6,7,8-HpCDF	67562-39-4	NA	8280A	NA	NA	NA
1,2,3,4,7,8,9-HpCDF	55673-89-7	NA	8280A	NA	NA	NA
OCDF	39001-02-0	NA	8280A	NA	NA	NA
2,3,7,8-TCDD	1746-01-6	NA	8290	NA	NA	NA
1,2,3,7,8-PeCDD	40321-76-4	NA	8290	NA	NA	NA
1,2,3,4,7,8-HxCDD	39227-28-6	NA	8290	NA	NA	NA
1,2,3,6,7,8-HxCDD	57653-85-7	NA	8290	NA	NA	NA
1,2,3,7,8,9-HxCDD	19408-74-3	NA	8290	NA	NA	NA
1,2,3,4,6,7,8-HpCDD	35822-39-4	NA	8290	NA	NA	NA
OCDD	3268-87-9	NA	8290	NA	NA	NA
2,3,7,8-TCDF	51207-31-9	NA	8290	NA	NA	NA
1,2,3,7,8-PeCDF	57117-41-6	NA	8290	NA	NA	NA
2,3,4,7,8-PeCDF	57117-31-4	NA	8290	NA	NA	NA
1,2,3,4,7,8-HxCDF	70648-26-9	NA	8290	NA	NA	NA
1,2,3,6,7,8-HxCDF	57117-44-9	NA	8290	NA	NA	NA
2,3,4,6,7,8-HxCDF	60851-34-5	NA	8290	NA	NA	NA
1,2,3,7,8,9-HxCDF	72918-21-9	NA	8290	NA	NA	NA
1,2,3,4,6,7,8-HpCDF	67562-39-4	NA	8290	NA	NA	NA
1,2,3,4,7,8,9-HpCDF	55673-89-7	NA	8290	NA	NA	NA
OCDF	39001-02-0	NA	8290	NA	NA	NA

Notes:
1. Table summarizes proposed analytical methods and data quality objectives (DQOs).
2. Investigation DQOs correspond to the higher of the soil screening level or the reporting limit (RL) for each analyte.
3. Method detection limits (MDLs) and reporting limits (RLs) shown are based on data provided by STL Savannah. Analytical methods are referenced from "Test Methods for Evaluating Solid Wastes, SW-846, Update III, 3rd edition," December 1996.
4. Applicable results will be reported as estimated value between method detection limit (MDL) and the reporting limit (RL).
5. Laboratory MDLs are continuously being evaluated and may differ slightly from these values.
6. Prep. = Digestion or extraction method.
   Det. = Determinative method for quantitation.
   NAPL = Non aqueous phase liquid
   DQL = Data quality level
   — = No value specified.
   NA = Not applicable to this constituent or not available.
   PQL = Practical quantitation limit

TABLE 1.4
ANALYTICAL PARAMETERS FOR SOIL CORES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analysis	**Analytical Method**
Physical Properties	
Free Product Mobility: Centrifuge Method	API RP 40 / ASTM D425M
Fluid Saturation: Dean Stark Method	API RP 40
Total Porosity	API RP 40
Grain Density	API RP 40
Bulk Density	API RP 40 / D2937-94
Viscosity	ASTM D445
Surface and Interfacial Tension	ASTM D971
Particle Size	ASTM D422-63
Air-Filled Porosity	API RP 40

Notes:
1. Physical properties analysis will be performed by PTS Geolabs, Houston, Texas, in accordance with ASTM and API standards.

2

2.0 PROJECT ORGANIZATION AND RESPONSIBILITY

2.1 Project Organizational Chart

Solutia Inc., has overall responsibility for implementation of the Work Plan for DNAPL Characterization and Remediation Study as directed by the U.S. EPA Project Coordinator. Working under contract to Solutia, Groundwater Services, Inc. (GSI), of Houston, Texas, will perform the field investigation and prepare the final report. Severn Trent Laboratories, Inc., in Savannah, Georgia will provide laboratory services for analysis of chemicals of concern (COCs), and PTS Geolabs, Inc. (PTS), in Houston, Texas, will analyze soil cores and NAPL for physical properties. Responsibilities for project management, quality assurance, laboratory, and field personnel are defined below and depicted on Figure 2.1.

2.2 Management Responsibilities

U.S. EPA Project Coordinator: The U.S. EPA Project Coordinator will have the overall responsibility for all phases of the study.

Solutia Inc. Project Manager: The Solutia Project Manager will be responsible for implementing the project, and will be accorded the authority to commit the resources necessary to meet project objectives. The primary function of the Solutia Project Manager will be to ensure that technical, financial, and scheduling objectives are achieved. Reporting directly to the U.S. EPA Project Coordinator, the Solutia Project Manager will serve as the major point of contact and control for matters concerning the project. The Solutia project manager, supported by the GSI Project Manager and other GSI personnel will:

- Define project objectives and develop a detailed work plan schedule;
- Establish project policy and procedures to address the specific needs of the project;
- Acquire and apply corporate and technical resources as needed to ensure performance within budget and schedule constraints;
- Orient field personnel and support staff to the project's special considerations;
- Review the work performed on each task to ensure quality, responsiveness, and timeliness;
- Review and analyze work performed relative to planned requirements and authorizations;
- Approve reports and deliverables before submittal to U.S. EPA Region 5;
- Retain ultimate responsibility for preparation and quality of interim and final reports; and
- Represent the project team at meetings.

GSI Project Manager: The GSI Project Manager will have overall responsibility for ensuring that the project meets the objectives and relevant quality standards of Solutia and U.S. EPA. The GSI Project Manager will provide assistance to the Solutia Project Manager in preparing and distributing project reports, including the QAPP, to parties

parties connected with the project, including the laboratory. The GSI Project Manager will report directly to the Solutia Project Manager.

2.3 Advisory and Technical Responsibilities

GSI Technical Advisor: Senior-level technical advisors will provide expertise on specific and general issues relating to the study, particularly DNAPL presence and mobility. In order to ensure that the appropriate type and quality of data is being collected, the GSI Technical Advisor will review and provide input on work plans and reports generated by the GSI Project Manager and Technical Staff during the project. Technical advisors will also be consulted in critical areas where proven and experienced technical support is needed.

GSI Health and Safety Officer: The GSI Health and Safety Officer will be responsible for overall health and safety practices associated with the field work. Specific functions and duties will include the following tasks:

- Establish the requirements of the project Health and Safety Plan (HASP);
- Arrange or conduct audits of field activities to ensure that proper health and safety procedures are being used;
- Communicate with the GSI Project Manager, GSI Field Operations Manager, and GSI Field Technical Staff concerning project issues related to health and safety.

GSI Technical Staff: The GSI Technical Staff will report to the GSI Project Manager and will assist with preparation of project reports and the QAPP.

2.4 Quality Assurance Responsibilities

U.S. EPA Region 5 Quality Assurance (QA) Manager: The U.S. EPA QA Manager will have the responsibility for review and approval of the Quality Assurance Project Plan (QAPP). Additional responsibilities for the project will include i) conducting external performance and system audits, and ii) reviewing and evaluating analytical field and laboratory procedures. The U.S. EPA QA Manager will report to the U.S. EPA Project Coordinator.

GSI QA Manager: The GSI QA Manager will report directly to the GSI Project Manager and will be responsible for i) preparing the QAPP, ii) reviewing QA documentation to evaluate compliance with sampling and analytical procedures, iii) ensuring that internal performance audits are conducted for field procedures, and iv) ensuring that validation is performed by the third party validation subcontractor on laboratory data packages for target parameters.

Data Validation Subcontractor: ECS Environmental Chemistry Services will be responsible for third-party validation of laboratory data generated during analysis of soil samples analyzed for VOCs and SVOCs, and NAPL samples analyzed for VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin and metals (including mercury) in accordance with USEPA SW-846 methods.

2.5 Laboratory Responsibilities

STL Project Manager: The STL Project Manager will report to the GSI Project Manager. The STL Project Manager will be responsible for ensuring laboratory resources are available to Solutia as needed for the project and will provide oversight of final laboratory reports.

STL QA Manager: The STL QA Manager will have overall responsibility for data generated in the laboratory. The STL QA Manager will be independent of the laboratory production responsibilities, but will communicate data issues through the STL Project Manager. In addition, the STL QA Manager will

- Monitor the day-to-day quality of the laboratory data.
- Maintain and review all quality control data.
- Conduct internal performance and system audits to ensure compliance with laboratory protocols.
- Review and maintain updated Standard Operating Procedures (SOPs).
- Prepare Performance Evaluation reports and corrective action reports.

STL Technical Staff: The STL Technical Staff will be responsible for sample analysis and identification of necessary corrective actions. Staff members will report directly to the STL Project Manager.

PTS Project Manager: The PTS Project Manager will report to the GSI Project Manager. The PTS Project Manager will be responsible for ensuring laboratory resources are available to Solutia as needed for the project and will provide oversight of final laboratory reports.

PTS QA Manager: The PTS QA Manager will have overall responsibility for data generated in the laboratory. The PTS Project Manager will be independent of the laboratory production responsibilities, but will communicate data issues through the PTS Project Manager. In addition, the PTS Project and QA Manager will

- Monitor the day-to-day quality of the laboratory data.
- Maintain and review all quality control data.
- Conduct internal performance and system audits to ensure compliance with laboratory protocols.
- Review and maintain updated SOPs.
- Prepare Performance Evaluation reports and corrective action reports.

PTS Technical Staff: The PTS Technical Staff will be responsible for sample analysis and identification of necessary corrective actions. Staff members will report directly to the PTS Project and QA Manager.

2.6 Field Responsibilities

GSI Field Operations Manager: The GSI Project Manager will be supported by the GSI Field Operations Manager who will lead and coordinate day-to-day field activities of

GSI Field Technical Staff and Field Investigation Subcontractor. The Field Operations Manager will also:

- Coordinate with the Solutia Project Manager on technical issues in specific areas of expertise;
- Implement field-related work plans;
- Coordinate and manage field staff for sampling and drilling activities;
- Implement QC for technical data obtained by field staff including field measurement data;
- Adhere to work schedules provided by the GSI Project Manager;
- Coordinate and oversee subcontractors assisting the GSI Field Technical Staff;
- Assist and instruct field personnel in set-up of decontamination lines and implementation of procedures in accordance with the project HASP;
- Identify problems at the field team level and implement corrective actions; and
- Participate in preparation of the final project report.

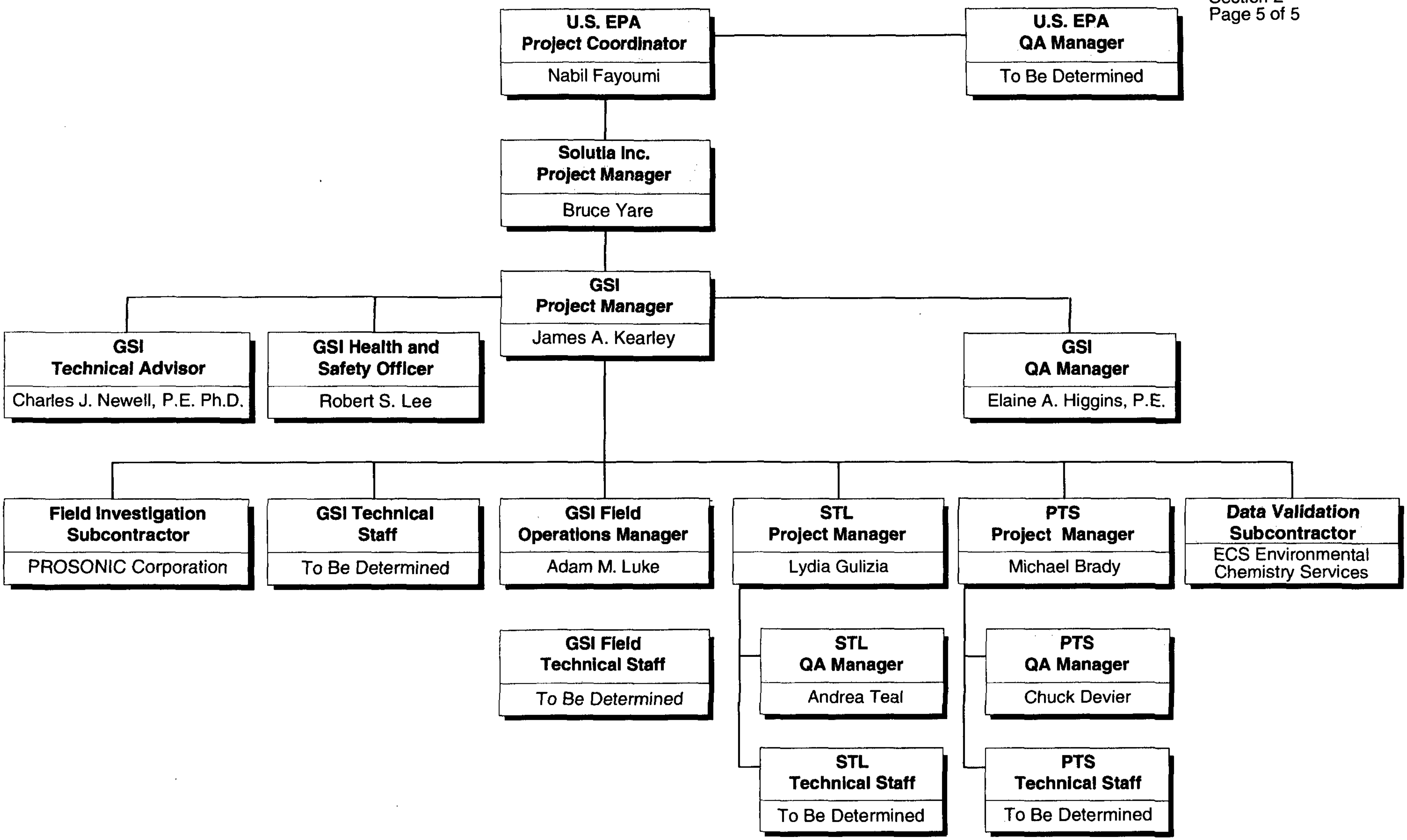
GSI Field Technical Staff: The GSI Technical Field Staff will assist the GSI Field Operations Manager in collecting soil samples and soil cores, performing field analyses, and recording field measurements.

Field Investigation Subcontractor: In order to achieve project objectives, GSI will obtain the services of PROSONIC Corporation to conduct drilling activities.

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

FIGURES



GROUNDWATER SERVICES, INC.

GSI Job No.	G-2876	Drawn By:	EAH
Issued:	4/01/04	Chk'd By:	EAH
Revised:		Aprv'd By:	JAK
Scale:	Not to Scale		FIGURE 2.1

PROJECT ORGANIZATIONAL CHART

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites, Sauget, Illinois

3.0 QUALITY ASSURANCE OBJECTIVES FOR MEASUREMENT DATA

In order to provide technically sound and defensible results, data quality objectives (DQOs) have been developed for the laboratory analysis of COC concentrations, soil properties, core properties, and treatability tests during the DNAPL Study. DQOs have been developed with a consideration of i) the level of data usage (i.e., definitive or screening) and ii) the level of detail available in the reference method to be used for analysis. Consequently, detailed DQOs have been developed for definitive data produced during analysis of COC concentrations in accordance with USEPA SW-846 methods, and a limited set of DQOs has been developed for data produced during analysis of core properties, treatability tests, and soil properties by API or ASTM methods.

For the analysis of COC concentrations by USEPA SW-846 methods, quantifiable DQOs have been developed for accuracy, precision, and completeness. Precision and accuracy DQOs for laboratory analyses have been developed on the basis of historical recovery and relative percent difference data obtained from STL Savannah (see Table 3.1). Acceptable levels of non-quantifiable data quality parameters (i.e., representativeness and completeness) will be assured through the proper implementation of field and laboratory SOPs.

Definitions, development, and interpretation of DQO parameters and detection limits are presented below. SOPs for laboratory analyses are provided in Appendix A of this QAPP. SOPs for field measurements are outlined in the Field Sampling Plan that accompanies this QAPP.

3.1 Precision

3.1.1 Definition

Precision is a measure of the degree to which two or more measurements are in agreement as a result of repeated application of a process under specific conditions. The overall precision and reproducibility of a measurement system is affected by variations introduced by sampling and analysis.

3.1.2 Field Precision Objectives

Field precision will be assessed by collecting and analyzing field duplicates at a rate of 1 duplicate per 10 analytical samples. The field precision objective for laboratory analysis of VOCs and SVOCs is ±30% relative percent difference (RPD) between field duplicates. No other analyses will have field precision objectives.

3.1.3 Laboratory Precision Objectives

Laboratory precision objectives for laboratory QC samples are listed on Table 3.1. Precision objectives for analysis of VOCs and SVOCs on listed on Table 3.2. In accordance with method requirements, laboratory precision will be assessed by analysis of various duplicates sets (i.e., laboratory duplicates, reagent water blank spike duplicates, matrix spike duplicates).

3.2 Accuracy

3.2.1 Definition

Accuracy is the degree of agreement between an observed value (or an average of several values) and an accepted reference value. Deviations from standard values result from cumulative inconsistencies in the measurement system. Potential sources of variance include (but are not limited to) sample collection, preservation, and handling procedures; matrix effects, and analytical procedures.

3.2.2 Field Accuracy Objectives

Accuracy in the field will be assessed through the use of field and trip blanks and through the adherence to all sample handling, preservation, and holding times). One trip blank will be submitted for laboratory analysis each day that samples are submitted for analysis of VOC concentration (see Table 3.4). An exception to this criterion will be that no trip blanks will be analyzed if NAPL is the only medium sampled. Accuracy objectives for field samples will be met if concentrations of VOCs and SVOCs are below project quantitation limits in the trip blank.

3.2.3 Laboratory Accuracy Objectives

In accordance with method requirements, laboratory accuracy will be assessed by the analysis of various spike samples (i.e., spikes, matrix spikes, control standards, interference check samples, standard reference samples, and surrogates). Where required by the method, an LCS will consist of a standard purchased from a source other than that for the calibration standards. The use of an LCS will be based on the availability of a USEPA, National Institute of Standards and Testing (NIST), or commercially certified LCS. Accuracy objectives for laboratory samples will be met if percent recoveries fall within the limits shown on Tables 3.2 and 3.3.

3.3 Completeness

3.3.1 Definition

Completeness is expressed as the percentage of valid data points obtained from a measurement system or method.

3.3.2 Field Completeness Objectives

Field completeness will be assessed for target parameters by comparing the number of valid field samples to the total number of field samples collected. The validity of field samples will be assessed by comparison of documented field practices to requirements of this QAPP and the accompanying Field Sampling Plan. The completeness objective for field samples will be at least 90%.

3.3.3 Laboratory Completeness Objectives

The results of a laboratory analysis will be considered valid if predetermined data quality objective standards are met or exceeded for precision and accuracy. A formal data validation, as described in Section 9 of this QAPP, will be conducted to assess completeness requirements on an analyte-by-analyte basis for VOCs and SVOCs analyzed in accordance with USEPA SW-846. Completeness requirements for other analytical parameters will be based on available QC data provided in accordance with applicable API and ASTM methods. Laboratory completeness will be assessed for COCs by comparing the number of valid measurements to the total number of measurements. Completeness for laboratory samples will be at least 95%.

3.4 Representativeness

3.4.1 Definition

Representativeness is a qualitative parameter that expresses the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. As such, representativeness describes whether samples collected, or the aliquots selected by the laboratory for analysis, are sufficient in number, type, location, frequency, and size to be characteristic of the substance analyzed.

3.4.2 Measures to Ensure Representativeness of Field Data

The sampling network for this project has been designed to provide data representative of site conditions giving appropriate consideration to existing analytical data and the physical setting as discussed in the Project Work Plan. Field representativeness will be satisfied by following the sample collection procedures specified in the Field Sampling Plan. In addition, collection of duplicate samples will provide a measure of the variability of analyte present in a particular sample volume.

3.4.3 Measures to Ensure Representativeness of Laboratory Data

Representativeness in the laboratory will be ensured by using the proper analytical procedures, meeting sample holding times, and analyzing and assessing field duplicates.

3.5 Comparability

3.5.1 Definition

Comparability is an expression of the confidence with which one data set can be compared with another.

3.5.2 Measures to Ensure Comparability of Field Data

Comparability of field data will be assured by adhering to standard sampling procedures described in the Field Sampling Plan, using traceable calibration standards; using standard measurement and reporting units; and using the pre-determined acceptance criteria for precision and accuracy presented in this QAPP.

3.5.3 Measures to Ensure Comparability of Laboratory Data

Comparability of laboratory data will be assured by adhering to standard analytical procedures described in this QAPP, using traceable calibration standards; using standard measurement and reporting units; and using pre-determined acceptance criteria for precision and accuracy.

3.6 Level of Quality Control Effort

3.6.1 Level of Field Quality Control Effort

Requirements for collection of field quality control samples are provided on Table 3.4. Field precision will be assessed by collecting and analyzing field duplicate samples. Matrix effects on the sample analysis will be assessed through the collection and analysis of matrix spikes and duplicates. As specified in the Field Sampling Plan, additional sample volumes will be collected in order to prepare MS/MSD sets for soil, NAPL, and water samples.

Sampling accuracy will be assessed by collecting and analyzing trip and equipment blanks. Results from the analysis of trip blanks will be used to assess the potential for sample contamination during sample shipment, handling, and storage. To assess potential sources of contamination resulting from sample collection activities and equipment decontamination, field equipment blanks will be collected only when employing re-usable sampling devices.

3.6.2 Level of Laboratory Quality Control Effort

Requirements for laboratory QC samples are provided on Table 3.1. Results from method blank samples for all constituents analyzed will be reviewed to assess potential sources of contamination associated with laboratory procedures. Laboratory method blanks will be prepared and analyzed at a frequency of 1 per sample batch (i.e., each group of samples prepared and analyzed as a group, not to exceed 20 samples).

Results for MS/MSD pairs will be reviewed to evaluate the effect of the sample matrix on the sample preparation and measurement methodology. MS/MSD sets will be analyzed at a frequency of 1 per sample batch (i.e., each group of samples prepared and analyzed as a group, not to exceed 20 samples). Recovery and relative percent difference targets for MS/MSD sets are listed on Table 3.2.

Accuracy for the analysis of volatile and semi-volatile organic compounds will be assessed by evaluating the recoveries of surrogate compounds spiked into all samples. Laboratory control limits for surrogates are provided on Table 3.3 of this QAPP.

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

TABLES

TABLE 3.1
PRECISION AND ACCURACY OBJECTIVES FOR LABORATORY QC SAMPLES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Parameter	EPA Reference Method	QC Sample Type	Frequency	Data Quality Objectives			
				Precision (% RPD)		Accuracy	
				Aqueous	Solid	Aqueous	Solid
1. Volatile Organics	8260B	Method Blank	1 per 12 hr of analysis	NA	NA	Target Analytes <RL	Target Analytes <RL
		Laboratory Spike and Duplicate	1 per 20 samples	See Table 3.2	See Table 3.2	See Table 3.2	See Table 3.2
		Matrix Spike and Duplicate	1 per 20 samples	See Table 3.2	See Table 3.2	See Table 3.2	See Table 3.2
2. Semi-Volatile Organics	8270C	Method Blank	1 per 20 samples	NA	NA	Target Analytes <RL	Target Analytes <RL
Pesticides	8081A	Laboratory Spike and Duplicate	1 per 20 samples	See Table 3.2	See Table 3.2	See Table 3.3	See Table 3.3
Herbicides	8151A	Matrix Spike and Duplicate	1 per 20 samples	See Table 3.2	See Table 3.2	See Table 3.3	See Table 3.3
PCBs	8082A						
3. Metals	6010B	Method Blank	Pending	NA	See Table 3.2	NA	See Table 3.3
Mercury	7141A	Lab Control Standard and Duplicate	Pending	NA	Pending	NA	Pending
4. Dioxins and Furans	8280A	Pending	Pending	NA	Pending	NA	Pending
5. Total Organic Carbon	SW-9060 (aq)	Method Blank	1 per 20 samples	NA	NA	Target Analyte <RL	Target Analyte <RL
		Matrix Spike and Duplicate	1 per 20 samples	< 20% RPD	NA	80-120 %R	NA
	EPA-CE (soil)	Lab Control Standard and Duplicate	1 per 20 samples	< 20% RPD	< 40% RPD	80-120 %R	60-140 %R
6. Total Porosity	API RP 40	Lab Control Standard	NA	NA	NA	NA	±0.02% Pore Volume
7. Bulk Density	ASTM D2937	Lab Control Standard	NA	NA	NA	NA	±0.5 of 1 Porosity %
8. Grain Density	API RP 40	Lab Control Standard	NA	NA	NA	NA	±0.5 of 1 Porosity %
9. Total Organic Carbon	Walkley Black	Method Blank	NA	NA	NA	NA	±3.0% Method Response Factor
		Lab Control Standard and Duplicate	NA	NA	±30% Initial Value	NA	±30% Certified Value
10. Fluid Saturation	API RP 40	Lab Control Standard	NA	NA	NA	NA	±0.02% Pore Volume

Notes:
1. STL Savannah Standard Operating Procedures (SOPs) and PTS methods provided in Appendix A of the QAPP.
2. Precision objectives represent relative percent difference (% RPD) between duplicates.
3. Samples, standards, and quality control (QC) samples analyzed for volatile and semi-volatile organics will be spiked with surrogates (see Table 3.3).
4. NA = Precision/accuracy data quality objective not applicable to this QC sample.
   RL = Reporting limit.
   RPD = Relative percent difference

GROUNDWATER SERVICES, INC.

TABLE 3.2
PRECISION AND ACCURACY OBJECTIVES FOR CONSTITUENTS
QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method: Prep. Solid	Analytical Method: Prep. Aqueous	Analytical Method: Det	Accuracy (%Rec) Solid	Accuracy (%Rec) Waste	Accuracy (%Rec) Aqueous	Precision (% RPD) Solid	Precision (% RPD) Waste	Precision (% RPD) Aqueous
Volatile Organics										
Acetone	67-64-1	5035	5030B	8260B	30-195	30-195	32-164	≤ 100	≤ 100	≤ 50
Benzene (MS)	71-43-2	5035	5030B	8260B	65-130	65-130	69-128	≤ 50	≤ 50	≤ 30
Bromodichloromethane	75-27-4	5035	5030B	8260B	71-120	71-120	69-134	≤ 50	≤ 50	≤ 30
Bromoform	75-25-2	5035	5030B	8260B	58-134	58-134	69-138	≤ 50	≤ 50	≤ 30
Bromomethane	74-83-9	5035	5030B	8260B	22-184	22-184	22-184	≤ 100	≤ 100	≤ 50
Carbon disulfide	75-15-0	5035	5030B	8260B	43-143	43-143	55-140	≤ 50	≤ 50	≤ 30
Carbon tetrachloride (MS)	56-23-5	5035	5030B	8260B	66-128	66-128	67-136	≤ 50	≤ 50	≤ 30
Chlorobenzene (MS)	108-90-7	5035	5030B	8260B	69-128	69-128	72-126	≤ 50	≤ 50	≤ 30
Chloroethane	75-00-3	5035	5030B	8260B	46-152	46-152	40-158	≤ 100	≤ 100	≤ 50
Chloroform	67-66-3	5035	5030B	8260B	70-124	70-124	72-124	≤ 50	≤ 50	≤ 30
Chloromethane	74-87-3	5035	5030B	8260B	42-143	42-143	40-123	≤ 100	≤ 100	≤ 50
Dibromochloromethane	124-48-1	5035	5030B	8260B	70-124	70-124	72-132	≤ 50	≤ 50	≤ 30
Dichloroethane, 1,1-	75-34-3	5035	5030B	8260B	34-166	34-166	41-158	≤ 50	≤ 50	≤ 30
Dichloroethane, 1,2-	107-06-2	5035	5030B	8260B	39-158	39-158	61-143	≤ 50	≤ 50	≤ 30
Dichloroethene, 1,1- (MS)	75-35-4	5035	5030B	8260B	46-142	46-142	53-144	≤ 50	≤ 50	≤ 30
Dichloroethene, cis-1,2-	156-59-2	5035	5030B	8260B	33-150	33-150	57-132	≤ 50	≤ 50	≤ 30
Dichloroethene, trans-1,2-	156-60-6	5036	5030B	8260B	23-160	23-159	48-149	≤ 50	≤ 50	≤ 30
Dichloropropane, 1,2-	78-87-5	5035	5030B	8260B	72-118	72-118	74-122	≤ 50	≤ 50	≤ 30
Dichloropropene, cis-1,3-	10061-01-5	5035	5030B	8260B	71-123	71-123	77-127	≤ 50	≤ 50	≤ 30
Dichloropropene, trans-1,3-	10061-02-6	5035	5030B	8260B	66-128	66-128	73-133	≤ 50	≤ 50	≤ 30
Ethylbenzene	100-41-4	5035	5030B	8260B	71-120	71-120	76-120	≤ 50	≤ 50	≤ 30
Hexanone, 2-	591-78-6	5035	5030B	8260B	46-163	46-163	43-158	≤ 50	≤ 50	≤ 30
Methyl ethyl ketone (MEK, 2-Butanone)	78-93-3	5035	5030B	8260B	30-185	30-185	38-153	≤ 50	≤ 50	≤ 30
Methyl-2-pentanone, 4- (MIBK)	108-10-1	5035	5030B	8260B	47-160	47-160	46-156	≤ 50	≤ 50	≤ 30
Methylene chloride	75-09-2	5035	5030B	8260B	29-153	29-153	63-133	≤ 100	≤ 100	≤ 50
Styrene	100-42-5	5035	5030B	8260B	73-121	73-121	75-123	≤ 50	≤ 50	≤ 30
Tetrachloroethane, 1,1,2,2-	79-34-5	5035	5030B	8260B	59-138	59-138	61-139	≤ 50	≤ 50	≤ 30
Tetrachloroethene	127-18-4	5035	5030B	8260B	64-134	64-134	71-129	≤ 50	≤ 50	≤ 30
Toluene (MS)	108-88-3	5035	5030B	8260B	63-133	63-133	71-129	≤ 50	≤ 50	≤ 30
Trichloroethane, 1,1,1-	71-55-6	5035	5030B	8260B	70-123	70-123	68-135	≤ 50	≤ 50	≤ 30
Trichloroethane, 1,1,2-	79-00-5	5035	5030B	8260B	66-127	66-127	70-129	≤ 50	≤ 50	≤ 30
Trichloroethene (MS)	79-01-6	5035	5030B	8260B	64-126	64-126	70-123	≤ 50	≤ 50	≤ 30
Vinyl chloride	75-01-4	5035	5030B	8260B	38-151	38-151	50-142	≤ 100	≤ 100	≤ 50
Xylenes (total)	1330-20-7	5035	5030B	8260B	74-122	74-122	77-121	≤ 50	≤ 50	≤ 30
Semi-Volatile Organics										
Acenaphthene (MS)	83-32-9	3550B	3510C/3520C	8270C	39-104	39-104	53-116	≤ 50	≤ 50	≤ 40
Acenaphthylene	208-96-8	3550B	3510C/3520C	8270C	37-112	37-112	52-121	≤ 50	≤ 50	≤ 40
Anthracene	120-12-7	3550B	3510C/3520C	8270C	34-120	34-120	54-126	≤ 50	≤ 50	≤ 40
Benzo(a)anthracene	56-55-3	3550B	3510C/3520C	8270C	28-134	28-134	54-131	≤ 50	≤ 50	≤ 40
Benzo(a)pyrene (MS)	50-32-8	3550B	3510C/3520C	8270C	30-128	30-128	43-132	≤ 50	≤ 50	≤ 40
Benzo(b)fluoranthene	205-99-2	3550B	3510C/3520C	8270C	29-128	29-128	45-136	≤ 50	≤ 50	≤ 40
Benzo(g,h,i)perylene	191-24-2	3550B	3510C/3520C	8270C	33-122	33-122	34-145	≤ 50	≤ 50	≤ 40
Benzo(k)fluoranthene	207-08-9	3550B	3510C/3520C	8270C	25-127	25-127	41-143	≤ 50	≤ 50	≤ 40
Bis(2-chloroethyl)ether	111-44-4	3550B	3510C/3520C	8270C	27-96	27-96	43-111	≤ 50	≤ 50	≤ 40
Bis(2-chloroethoxy)methane	111-91-1	3550B	3510C/3520C	8270C	34-102	34-102	57-110	≤ 50	≤ 50	≤ 40
Bis(2-ethylhexyl)phthalate	117-81-7	3550B	3510C/3520C	8270C	39-122	39-122	57-126	≤ 50	≤ 50	≤ 40
Bromophenyl phenyl ether, 4-	101-55-3	3550B	3510C/3520C	8270C	33-94	33-94	45-106	≤ 50	≤ 50	≤ 40
Butyl benzyl phthalate	85-68-7	3550B	3510C/3520C	8270C	44-121	44-121	58-129	≤ 50	≤ 50	≤ 40
Carbazole	86-74-8	3550B	3510C/3520C	8270C	26-129	NA	39-126	≤ 50	NA	≤ 40
Chloro-3-methylphenol, 4- (MS)	59-50-7	3550B	3510C/3520C	8270C	22-124	22-124	53-117	≤ 50	≤ 50	≤ 40
Chloroaniline, 4-	106-47-8	3550B	3510C/3520C	8270C	18-94	18-94	10-95	≤ 50	≤ 50	≤ 40
Chloronaphthalene, 2-	91-58-7	3550B	3510C/3520C	8270C	42-96	42-96	54-104	≤ 50	≤ 50	≤ 40
Chlorophenol, 2- (MS)	95-57-8	3550B	3510C/3520C	8270C	22-109	22-109	43-110	≤ 50	≤ 50	≤ 40
Chlorophenyl phenyl ether, 4-	7005-72-3	3550B	3510C/3520C	8270C	38-101	38-101	47-119	≤ 50	≤ 50	≤ 40
Chrysene	218-01-9	3550B	3510C/3520C	8270C	35-130	35-130	52-135	≤ 50	≤ 50	≤ 40
Cresol, m- (Methyl phenol, 2-)	108-39-4	3550B	3510C/3520C	8270C	35-102	34-108	40-116	≤ 50	≤ 50	≤ 40
Cresol, o- (Methyl phenol, 3-)	95-48-7	3550B	3510C/3520C	8270C	34-108	35-102	48-113	≤ 50	≤ 50	≤ 40
Cresol, p- (Methyl phenol, 4-)	106-44-5	3550B	3510C/3520C	8270C	35-102	35-102	40-116	≤ 50	≤ 50	≤ 40
Di-n-octyl phthalate	84-74-2	3550B	3510C/3520C	8270C	38-126	38-126	56-127	≤ 50	≤ 50	≤ 40
Di-n-butyl phthalate	117-84-0	3550B	3510C/3520C	8270C	39-116	39-116	53-131	≤ 50	≤ 50	≤ 40
Dibenz(a,h)anthracene	53-70-3	3550B	3510C/3520C	8270C	29-126	29-126	42-136	≤ 50	≤ 50	≤ 40
Dibenzofuran	132-64-9	3550B	3510C/3520C	8270C	34-112	34-112	57-113	≤ 50	≤ 50	≤ 40
Dichlorobenzene, 1,2-	95-50-1	3550B	3510C/3520C	8270C	31-86	31-86	33-99	≤ 50	≤ 50	≤ 40
Dichlorobenzene, 1,3-	541-73-1	3550B	3510C/3520C	8270C	33-81	33-81	31-95	≤ 50	≤ 50	≤ 40
Dichlorobenzene, 1,4- (MS)	106-46-7	3550B	3510C/3520C	8270C	25-93	25-93	36-91	≤ 50	≤ 50	≤ 40

See last page of table for explanatory notes.

TABLE 3.2
PRECISION AND ACCURACY OBJECTIVES FOR CONSTITUENTS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

		Analytical Method								
	CAS	Prep.			Accuracy (%Rec)			Precision (% RPD)		
Analyte	Number	Solid	Aqueous	Det	Solid	Waste	Aqueous	Solid	Waste	Aqueous
Semi-Volatile Organics (continued)										
Dichlorobenzidine, 3,3'-	91-94-1	3550B	3510C/3520C	8270C	10-98	10-98	10-109	≤ 50	≤ 50	≤ 40
Dichlorophenol, 2,4-	120-83-2	3550B	3510C/3520C	8270C	37-103	37-103	47-115	≤ 50	≤ 50	≤ 40
Diethyl phthalate	84-66-2	3550B	3510C/3520C	8270C	37-112	37-112	58-120	≤ 50	≤ 50	≤ 40
Dimethyl phthalate	131-11-3	3550B	3510C/3520C	8270C	40-106	40-106	59-115	≤ 50	≤ 50	≤ 40
Dimethylphenol, 2,4-	105-67-9	3550B	3510C/3520C	8270C	45-99	45-99	38-114	≤ 50	≤ 50	≤ 40
Dinitro-2-methylphenol, 4,6-	534-52-1	3550B	3510C/3520C	8270C	D-134	24-128	10-118	≤ 100	≤ 50	≤ 40
Dinitrophenol, 2,4-	51-28-5	3550B	3510C/3520C	8270C	19-126	19-126	12-172	≤ 50	≤ 50	≤ 40
Dinitrotoluene (MS), 2,4-	121-14-2	3550B	3510C/3520C	8270C	18-125	18-125	44-129	≤ 50	≤ 50	≤ 40
Dinitrotoluene, 2,6-	606-20-2	3550B	3510C/3520C	8270C	42-109	42-109	57-126	≤ 50	≤ 50	≤ 40
Dinoseb	88-85-7	3550B	3510C/3520C	8270C	D-114	NA	10-127	≤ 50	NA	≤ 40
Fluoranthene	206-44-0	3550B	3510C/3520C	8270C	18-137	18-137	47-136	≤ 50	≤ 50	≤ 40
Fluorene	86-73-7	3550B	3510C/3520C	8270C	35-112	35-112	49-126	≤ 50	≤ 50	≤ 40
Hexachlorobenzene	118-74-1	3550B	3510C/3520C	8270C	34-103	34-103	39-125	≤ 50	≤ 50	≤ 40
Hexachlorobutadiene	87-68-3	3550B	3510C/3520C	8270C	35-98	35-98	35-106	≤ 50	≤ 50	≤ 40
Hexachlorocyclopentadiene	77-47-4	3550B	3510C/3520C	8270C	19-107	19-107	D-78	≤ 50	≤ 50	≤ 100
Hexachloroethane	67-72-1	3550B	3510C/3520C	8270C	29-84	29-84	27-93	≤ 50	≤ 50	≤ 40
Indeno(1,2,3-c,d)pyrene	193-39-5	3550B	3510C/3520C	8270C	24-136	24-136	29-150	≤ 50	≤ 50	≤ 40
Isophorone	78-59-1	3550B	3510C/3520C	8270C	34-103	34-103	49-120	≤ 50	≤ 50	≤ 40
Methylnaphthalene, 2-	91-57-6	3550B	3510C/3520C	8270C	37-108	37-108	46-116	≤ 50	≤ 50	≤ 40
Naphthalene	91-20-3	3550B	3510C/3520C	8270C	36-94	36-94	41-111	≤ 50	≤ 50	≤ 40
Nitroaniline, 2-	88-74-4	3550B	3510C/3520C	8270C	22-99	35-113	41-117	≤ 50	≤ 50	≤ 40
Nitroaniline, 3-	99-09-2	3550B	3510C/3520C	8270C	32-111	22-99	42-132	≤ 50	≤ 50	≤ 40
Nitroaniline, 4-	100-01-6	3550B	3510C/3520C	8270C	24-110	32-111	49-107	≤ 50	≤ 50	≤ 40
Nitrobenzene	98-95-3	3550B	3510C/3520C	8270C	10-100	24-110	10-112	≤ 50	≤ 50	≤ 40
Nitrophenol, 2-	88-75-5	3550B	3510C/3520C	8270C	33-102	33-102	43-121	≤ 50	≤ 50	≤ 40
Nitrophenol, 4- (MS)	100-02-7	3550B	3510C/3520C	8270C	13-133	13-133	38-131	≤ 50	≤ 50	≤ 40
Nitrosodiphenylamine, N-	86-30-6	3550B	3510C/3520C	8270C	17-110	16-113	30-130	≤ 50	≤ 50	≤ 40
Nitroso-di-n-propylamine, N- (MS)	621-64-7	3550B	3510C/3520C	8270C	16-113	17-110	42-117	≤ 50	≤ 50	≤ 40
Pentachlorophenol (MS)	87-86-5	3550B	3510C/3520C	8270C	17-140	17-140	49-126	≤ 50	≤ 50	≤ 40
Phenanthrene	85-01-8	3550B	3510C/3520C	8270C	34-123	34-123	56-128	≤ 50	≤ 50	≤ 40
Phenol (MS)	108-95-2	3550B	3510C/3520C	8270C	20-108	20-108	40-109	≤ 50	≤ 50	≤ 40
Pyrene (MS)	129-00-0	3550B	3510C/3520C	8270C	36-132	36-132	52-141	≤ 50	≤ 50	≤ 40
Trichlorobenzene, 1,2,4- (MS)	120-82-1	3550B	3510C/3520C	8270C	26-102	26-102	41-97	≤ 50	≤ 50	≤ 40
Trichlorophenol, 2,4,5-	95-95-4	3550B	3510C/3520C	8270C	44-110	44-110	51-118	≤ 50	≤ 50	≤ 40
Trichlorophenol, 2,4,6-	88-06-2	3550B	3510C/3520C	8270C	43-110	43-110	50-117	≤ 50	≤ 50	≤ 40
Metals										
Aluminum	7429-90-5	3050B	NA	6010B	75-125	75-125	NA	≤ 20	≤ 20	NA
Antimony	7440-36-0	3050B	NA	6010B	75-125	75-125	NA	≤ 20	≤ 20	NA
Arsenic	7440-38-2	3050B	NA	6010B	75-125	75-125	NA	≤ 20	≤ 20	NA
Barium	7440-39-3	3050B	NA	6010B	75-125	75-126	NA	≤ 20	≤ 20	NA
Beryllium	7440-41-7	3050B	NA	6010B	75-125	75-127	NA	≤ 20	≤ 20	NA
Cadmium	7440-43-9	3050B	NA	6010B	75-125	75-128	NA	≤ 20	≤ 20	NA
Calcium	7440-70-2	3050B	NA	6010B	75-125	75-129	NA	≤ 20	≤ 20	NA
Chromium	7440-47-3	3050B	NA	6010B	75-125	75-130	NA	≤ 20	≤ 20	NA
Cobalt	7440-48-4	3050B	NA	6010B	75-125	75-131	NA	≤ 20	≤ 20	NA
Copper	7440-50-8	3050B	NA	6010B	75-125	75-132	NA	≤ 20	≤ 20	NA
Iron	7439-89-6	3050B	NA	6010B	75-125	75-133	NA	≤ 20	≤ 20	NA
Lead	7439-92-1	3050B	NA	6010B	75-125	75-134	NA	≤ 20	≤ 20	NA
Magnesium	7439-95-4	3050B	NA	6010B	75-125	75-135	NA	≤ 20	≤ 20	NA
Mercury	7439-97-6	7471	7471	7471	80-120	80-120	NA	≤ 20	≤ 20	NA
Nickel	7440-02-0	3050B	NA	6010B	75-125	75-137	NA	≤ 20	≤ 20	NA
Potassium	7440-09-7	3050B	NA	6010B	75-125	75-138	NA	≤ 20	≤ 20	NA
Selenium	7782-49-2	3050B	NA	6010B	75-125	75-139	NA	≤ 20	≤ 20	NA
Silver	7440-22-4	3050B	NA	6010B	75-125	75-140	NA	≤ 20	≤ 20	NA
Sodium	7440-23-5	3050B	NA	6010B	75-125	75-141	NA	≤ 20	≤ 20	NA
Thallium	7440-28-0	3050B	NA	6010B	75-125	75-142	NA	≤ 20	≤ 20	NA
Vanadium	7440-62-2	3050B	NA	6010B	75-125	75-143	NA	≤ 20	≤ 20	NA
Zinc	7440-66-6	3050B	NA	6010B	75-125	75-144	NA	≤ 20	≤ 20	NA

See last page of table for explanatory notes.

TABLE 3.2
PRECISION AND ACCURACY OBJECTIVES FOR CONSTITUENTS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep. Solid	Analytical Method Prep. Aqueous	Analytical Method Det	Accuracy (%Rec) Solid	Accuracy (%Rec) Waste	Accuracy (%Rec) Aqueous	Precision (% RPD) Solid	Precision (% RPD) Waste	Precision (% RPD) Aqueous
Pesticides										
Aldrin	309-00-2	3580	NA	8081	10-144	34-124	NA	≤ 38	≤ 50	NA
alpha-BHC	319-84-6	3580	NA	8081	22-101	22-125	NA	≤ 40	≤ 50	NA
beta-BHC	319-85-7	3580	NA	8081	12-120	36-144	NA	≤ 40	≤ 50	NA
Gamma-BHC (Lindane)	58-89-9	3580	NA	8081	12-138	35-132	NA	≤ 37	≤ 50	NA
delta-BHC	319-86-8	3580	NA	8081	10-142	32-140	NA	≤ 47	≤ 50	NA
alpha Chlordane	5103-71-9	3580	NA	8081	45140	40-139	NA	≤ 40	≤ 50	NA
Gamma Chlordane	5103-74-2	3580	NA	8081	11-141	39-143	NA	≤ 40	≤ 50	NA
4,4'-DDD	72-54-8	3580	NA	8081	28-134	37-149	NA	≤ 50	≤ 50	NA
4,4'-DDE	72-55-9	3580	NA	8081	34-121	33-139	NA	≤ 25	≤ 50	NA
4,4'-DDT	50-29-3	3580	NA	8081	29-134	46-156	NA	≤ 26	≤ 50	NA
Dieldrin	60-57-1	3580	NA	8081	28-137	40-133	NA	≤ 30	≤ 50	NA
Endosulfan I	959-98-8	3580	NA	8081	10-141	31-133	NA	≤ 40	≤ 50	NA
Endosulfan II	33213-65-9	3580	NA	8081	10-159	34-150	NA	≤ 65	≤ 50	NA
Endosulfan sulfate	1031-07-8	3580	NA	8081	26-144	45-163	NA	≤ 50	≤ 50	NA
Endrin	72-20-8	3580	NA	8081	33-149	42-137	NA	≤ 32	≤ 50	NA
Endrin aldehyde	7421-93-4	3580	NA	8081	10-130	37-152	NA	≤ 86	≤ 50	NA
Endrin ketone	53494-70-5	3580	NA	8081	29-112	44-165	NA	≤ 31	≤ 50	NA
Heptachlor	76-44-8	3580	NA	8081	17-138	31-142	NA	≤ 38	≤ 50	NA
Heptachlor epoxide	1024-57-3	3580	NA	8081	15-142	29-133	NA	≤ 40	≤ 50	NA
Methoxychlor	72-43-5	3580	NA	8081	24-152	37-185	NA	≤ 40	≤ 50	NA
Toxaphene	8001-35-2	3580	NA	8081	41-126	36-159	NA	≤ 50	≤ 50	NA
Herbicides										
2,4-D	94-75-7	3580	NA	8151	19-153	NA	NA	≤ 47	NA	NA
Dalapon	75-99-0	3580	NA	8151	10-170	NA	NA	≤ 40	NA	NA
2,4-DB	94-82-6	3580	NA	8151	20-160	NA	NA	≤ 40	NA	NA
Dicamba	1918-00-9	3580	NA	8151	20-160	NA	NA	≤ 40	NA	NA
Dichloroprop	120-36-5	3580	NA	8151	30-170	NA	NA	≤ 40	NA	NA
MCPA	94-74-6	3580	NA	8151	10-130	NA	NA	≤ 50	NA	NA
MCPP	7085-19-0/ 93-65-2	3580	NA	8151	10-130	NA	NA	≤ 50	NA	NA
Pentachlorophenol	87-86-5	3580	NA	8151	10-150	NA	NA	≤ 40	NA	NA
2,4,5-T	93-76-5	3580	NA	8151	14-143	NA	NA	≤ 59	NA	NA
2,4,5-TP (Silvex)	93-72-1	3580	NA	8151	27-120	NA	NA	≤ 51	NA	NA
PCBs										
Aroclor 1016	NA	3580	NA	8082	NA	24-132	NA	NA	≤ 50	NA
Aroclor 1221	NA	3580	NA	8082	NA	30-130	NA	NA	≤ 50	NA
Aroclor 1232	NA	3580	NA	8082	NA	30-130	NA	NA	≤ 50	NA
Aroclor 1242	NA	3580	NA	8082	NA	30-130	NA	NA	≤ 50	NA
Aroclor 1248	NA	3580	NA	8082	NA	30-150	NA	NA	≤ 50	NA
Aroclor 1254	NA	3580	NA	8082	NA	30-150	NA	NA	≤ 50	NA

See last page of table for explanatory notes.

GROUNDWATER SERVICES, INC.

TABLE 3.2
PRECISION AND ACCURACY OBJECTIVES FOR CONSTITUENTS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	CAS Number	Analytical Method Prep. Solid	Aqueous	Det	Accuracy (%Rec) Solid	Waste	Aqueous	Precision (% RPD) Solid	Waste	Aqueous
Dioxins and Furans										
2,3,7,8-TCDD	1746-01-6	NA	NA	8280A	66-139	NA	NA	≤ 50	NA	NA
1,2,3,7,8-PeCDD	40321-76-4	NA	NA	8280A	55-145	NA	NA	≤ 50	NA	NA
1,2,3,4,7,8-HxCDD	39227-28-6	NA	NA	8280A	50-150	NA	NA	≤ 50	NA	NA
1,2,3,6,7,8-HxCDD	57653-85-7	NA	NA	8280A	63-135	NA	NA	≤ 50	NA	NA
1,2,3,7,8,9-HxCDD	19408-74-3	NA	NA	8280A	50-150	NA	NA	≤ 50	NA	NA
1,2,3,4,6,7,8-HpCDD	35822-39-4	NA	NA	8280A	55-138	NA	NA	≤ 50	NA	NA
OCDD	3268-87-9	NA	NA	8280A	52-139	NA	NA	≤ 50	NA	NA
2,3,7,8-TCDF	51207-31-9	NA	NA	8280A	70-128	NA	NA	≤ 50	NA	NA
1,2,3,7,8-PeCDF	57117-41-6	NA	NA	8280A	59-137	NA	NA	≤ 50	NA	NA
2,3,4,7,8-PeCDF	57117-31-4	NA	NA	8280A	50-150	NA	NA	≤ 50	NA	NA
1,2,3,4,7,8-HxCDF	70648-26-9	NA	NA	8280A	50-150	NA	NA	≤ 50	NA	NA
1,2,3,6,7,8-HxCDF	57117-44-9	NA	NA	8280A	64-136	NA	NA	≤ 50	NA	NA
2,3,4,6,7,8-HxCDF	60851-34-5	NA	NA	8280A	50-150	NA	NA	≤ 50	NA	NA
1,2,3,7,8,9-HxCDF	72918-21-9	NA	NA	8280A	50-150	NA	NA	≤ 50	NA	NA
1,2,3,4,6,7,8-HpCDF	67562-39-4	NA	NA	8280A	73-130	NA	NA	≤ 50	NA	NA
1,2,3,4,7,8,9-HpCDF	55673-89-7	NA	NA	8280A	50-150	NA	NA	≤ 50	NA	NA
OCDF	39001-02-0	NA	NA	8280A	60-136	NA	NA	≤ 50	NA	NA
2,3,7,8-TCDD	1746-01-6	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,7,8-PeCDD	40321-76-4	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,4,7,8-HxCDD	39227-28-6	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,6,7,8-HxCDD	57653-85-7	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,7,8,9-HxCDD	19408-74-3	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,4,6,7,8-HpCDD	35822-39-4	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
OCDD	3268-87-9	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
2,3,7,8-TCDF	51207-31-9	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,7,8-PeCDF	57117-41-6	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
2,3,4,7,8-PeCDF	57117-31-4	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,4,7,8-HxCDF	70648-26-9	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,6,7,8-HxCDF	57117-44-9	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
2,3,4,6,7,8-HxCDF	60851-34-5	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,7,8,9-HxCDF	72918-21-9	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,4,6,7,8-HpCDF	67562-39-4	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
1,2,3,4,7,8,9-HpCDF	55673-89-7	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA
OCDF	39001-02-0	NA	NA	8290	60-140	NA	NA	≤ 20	NA	NA

Notes:
1. Laboratory control limits based upon data provided by STL Savannah.
2. STL Savannah Standard Operating Procedures (SOPs) for EPA reference methods are provided in Appendix A of this QAPP. Table 7.1 provides a list of STL Savannah SOPs corresponding to methods shown above.
3. N-Nitrosodiphenylamine (requires floracil cleanup to separate from Diphenylamine)
4. Dioxan and furan information provided by STL Sacramento.
5. Pesticides, herbicides, PCBs, Dioxins and furans are only performed on NAPL matrix only.
6. %Rec = Percent recovery. %RPD = Relative percent difference.
   a = Information is pending.

TABLE 3.3
LABORATORY CONTROL LIMITS FOR SURROGATES IN ANALYTICAL CONSTITUENTS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Analyte	EPA SW-846 Reference Method	Laboratory Control Limits for Percent Recovery Water (%)	Laboratory Control Limits for Percent Recovery Solid (%)
Volatile Organics			
p-Bromofluorobenzene	8260B	70-119	68-121
Dibromofluoromethane	8260B	68-129	66-127
Toluene-d8	8260B	74-122	65-128
Semi-Volatile Organics			
2-Fluorobiphenyl	8270C	55-116	37-106
2-Fluorophenol	8270C	43-114	31-105
Nitrobenzene-d5	8270C	51-115	31-99
Phenol-d5	8270C	46-112	31-105
Terphenyl-d14	8270C	11-120	38-120
2,4,6-Tribromophenol	8270C	47-133	26-127
Pesticides			
Tetrachloro-m-xylene (TCMX)	8081	NA	30-150
Decachlorobiphenyl (DCB)	8081	NA	30-150
Herbicides			
2,4-Dichlorophenyl acetic acid (DCAA)	8151	NA	30-189
PCBs			
Decachlorobiphenyl (DCB)	680	NA	30-130

Notes:
1. Control limits based upon historical data provided by STL Savannah.
2. Laboratory procedures will be conducted in accordance with the EPA reference methods shown above.
3. See Appendix A of this QAPP for laboratory SOPs, including surrogate spike concentrations for various sample concentration levels.

TABLE 3.4
REQUIREMENTS FOR FIELD QUALITY ASSURANCE SAMPLES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

QA Sample Type	Matrix	Laboratory Analytes	Preparation/Collection Method	Frequency	Data Quality Objectives
Field Duplicates	*Soil*	Volatile Organics Semi-Volatile Organics	Collect per FSP	1 per 10 samples	±30% RPD between duplicates
	Water	Volatile Organics Semi-Volatile Organics	Collect per FSP	1 per 10 samples	±30% RPD between duplicates
	NAPL	Volatile Organics Semi-Volatile Organics Organochlorine Pesticides Chlorinated Herbicides Polychlorinated Biphenyls Dioxins and Furans Metals	Collect per FSP	1 per 10 samples	±30% RPD between duplicates
Matrix Spike and Duplicates	*Soil*	Volatile Organics Semi-Volatile Organics	Collect per FSP	1 per 20 samples	See Table 3.2
	Water	Volatile Organics Semi-Volatile Organics	Collect per FSP	1 per 20 samples	See Table 3.2
Trip Blanks	*Soil*	Volatile Organics	3-40 mL glass vials filled with distilled water in laboratory prior to sampling	1 per day when soil or water is being sampled	Target Parameter Concentrations <RL
	Water	Volatile Organics	3-40 mL glass vials filled with distilled water in laboratory prior to sampling	1 per day when soil or water is being sampled	Target Parameter Concentrations <RL
Field Equipment Blanks (see Note 1)	*Soil*	Volatile Organics Semi-Volatile Organics	Run distilled water through decontaminated field equipment and collect in method-specified containers	1 per day during sample collection for each type of sample collection device	Target Parameter Concentrations <RL
	Water	Volatile Organics Semi-Volatile Organics	Run distilled water through decontaminated field equipment and collect in method-specified containers	1 per day during sample collection for each type of sample collection device	Target Parameter Concentrations <RL

Notes:
1. Field equipment blanks collected only when employing re-usable sampling devices requiring decontamination between samples.
2. RL = Reporting limit. FSP = Field Sampling Plan.
3. No QA samples will be collected or analyzed for total organic carbon.

4

4.0 SAMPLING PROCEDURES

Field sampling procedures employed during the DNAPL Study will be consistent throughout the project, thus providing data representative of site conditions, comparability with analytical considerations, practicality, and simplicity. Procedures for installation of soil borings and all aspects of collection, preservation, and transport of soil and core samples are provided in the Field Sampling Plan.

Method specified sample containers, preservatives, and holding times are summarized for soil and aqueous matrices on Table 4.1. Example forms for logging samples and/or cores, soil samples, soil borings, and water samples are provided on Figures 4.1 - 4.4. Typical piezometer construction details are shown on Figure 4.5.

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

TABLES

TABLE 4.1
SAMPLE CONTAINER, PRESERVATION, AND HOLDING TIME REQUIREMENTS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Parameter Group	Reference Method		Sample Container and Preservative			Sample Storage	Maximum Holding Time	
	Water	Soil/NAPL	Aqueous	Soil	NAPL		Extraction or Derivatization	Analysis after Extraction or Derivatization
Volatile Organics	8260B	5035 / 8260B	4 - 40 mL glass vials HCl to pH<2 headspace free	4 - 4 oz glass jar 125 mL amber glass jar (Note 2)	40 mL glass vial	4±2° C	NA	14 days
Semi-Volatile Organics	8270C	8270C	Two-1000 mL amber glass bottles	1 - 8 oz glass jar	250 mL glass jar	4±2° C	Water: 7 days Soil/NAPL: 14 days	40 days
Organochlorine Pesticides	NA	8081A	NA	NA	250 mL glass jar	4±2° C	14 days	40 days
Chlorinated Herbicides	NA	8151A	NA	NA	250 mL glass jar	4±2° C	14 days	40 days
Polychlorinated Biphenyls	NA	8082	NA	NA	250 mL glass jar	4±2° C	14 days	40 days
Dioxins and Furans	NA	8280A	NA	NA	250 mL glass jar	4±2° C	14 days	40 days
Metals (except mercury)								
All except mercury	NA	6010B	NA	NA	250 mL glass jar	4±2° C	NA	6 mo.
Mercury	NA	7470A	NA	NA	250 mL glass jar	4±2° C	NA	28 days
Total Organic Carbon	415 / 9060	EPA-CE Walkley-Black	125 mL amber glass bottle HCl to pH<2	250 mL HDPE bottle	NA	4±2° C	NA	28 days
Physical Properties								
Free Product Mobility: Centrifuge Method	NA	API & ASTM	NA	2" X 6" tube per sample	NA	NA	NA	NA
Fluid Saturation: Dean Stark Method	NA	API RP40	NA	2" X 6" tube per sample	NA	4±2° C	NA	NA
Total Porosity	NA	API RP40	NA	2" X 6" tube per sample	NA	4±2° C	NA	NA
Grain Density	NA	API RP40	NA	100 grams	NA		NA	NA
Bulk Density	NA	API RP40/ASTM D2937	NA	2" X 6" tube per sample	NA	4±2° C	NA	NA
Viscosity	NA	ASTM D445	NA	NA	500 ml headspace free container	NA	NA	NA
Surface and Interfacial Tension	NA	ASTM D2285	NA	NA	2 Liters of sample headspace free container	NA	NA	NA
Particle Size	NA	ASTM D422	NA	500 grams	NA	NA	NA	NA
Air-Filled Porosity	NA	API RP40	NA	2" X 6" tube per sample	NA	NA	NA	NA

Notes:
1. Laboratory procedures will be conducted in accordance with the reference methods specified above.
2. The solids sample collected in a 125-mL amber glass jar to be analyzed for volatile organics will be used for determining percent moisture, fraction organic carbon (Method 5310B), and soil pH (Method 9045C). Volatile soil samples will be preserved with 5 mL 5% sodium bisulfate for low-level analysis (3 subsamples) and with methanol for medium-level analysis (1 subsample).
3. Core samples sent to PTS labs will be shipped on dry ice.
4. Only NAPL samples will be anlayzed for organochlorine pesticides, chlorinated herbicides, polychlorinated biphenyls, dioxins and furans, and metals.
   NA = Not applicable to this analysis or matrix.

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

FIGURES

GEOLOGIST: ____________ COMPLETION DATE: ____________
DRILLER: ____________ GROUND SURFACE ELEV.: ____________
DRILLING METHOD: ____________ TOP OF CASING ELEV: ____________
HOLE DIAMETER: ____________ PLANT COORDINATES: ____________

DEPTH IN FEET	SAMPLE	BLOWS/FT	OVA (ppm)	USCS SYMBOL	SOIL DESCRIPTION
					GROUND SURFACE
0					
5					
10					
15					
20					
25					
30					
35					

Groundwater Services, Inc.
Houston, Texas

LOG OF SOIL BORING
____

Client: ____________

GSI Job No. ____________

Page ____________

GROUNDWATER SERVICES, INC.

EXAMPLE SAMPLE/CORE LOG

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1
Sauget, Illinois

FIGURE

4.1

GEOLOGIST: ____________ COMPLETION DATE: ____________
DRILLER: ____________ GROUND SURFACE ELEV.: ____________
DRILLING METHOD: ____________ TOP OF CASING ELEV: ____________
HOLE DIAMETER: ____________ PLANT COORDINATES: ____________

DEPTH IN FEET	SAMPLE	BLOWS/FT	OVA (ppm)	USCS SYMBOL	SOIL DESCRIPTION
					GROUND SURFACE
0					
5					
10					
15					
20					
25					
30					
35					

Groundwater Services, Inc.
Houston, Texas

LOG OF SOIL BORING ____________

Client: ____________

GSI Job No. ____________

Page ____________

GROUNDWATER SERVICES, INC.

EXAMPLE SOIL BORING LOG

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1
Sauget, Illinois

FIGURE

4.2

Well Installation Information:

Geologist: ______
Driller: ______
Drilling Method: ______
Completion Date: ______

Well Construction Specifications:

Casing Diam.	______	Sand Grade	______
Int. Casing	______	T/Sand Pack	______
Screen Slot	______	T/Pellets	______
Screen Depths	______	Qty. Water Added	______
Sump	______	Centralizer(s)	______

SOIL DESCRIPTION	DEPTH IN FEET	SAMPLE	BLOWS/FT	USCS	COMP. STR. (tsf)	OVA (ppm)	As-Built
GROUND SURFACE	0						
	5						
	10						
	15						
	20						
	25						
	30						

Continued on next page

Groundwater Services, Inc.
Houston, Texas

LOG & AS-BUILT DIAGRAM

______

Client: ______

GSI Job No. ______

Page ______

GROUNDWATER SERVICES, INC.

EXAMPLE WELL CONSTRUCTION LOG

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1
Sauget, Illinois

FIGURE

4.3

GROUNDWATER
SERVICES, INC.

GROUNDWATER SAMPLING RECORD

Client: ____________________ Date: ______________ GSI Job No. ______________

Project: ____________________ Personnel: ______________ Page ______________

SAMPLE INFORMATION

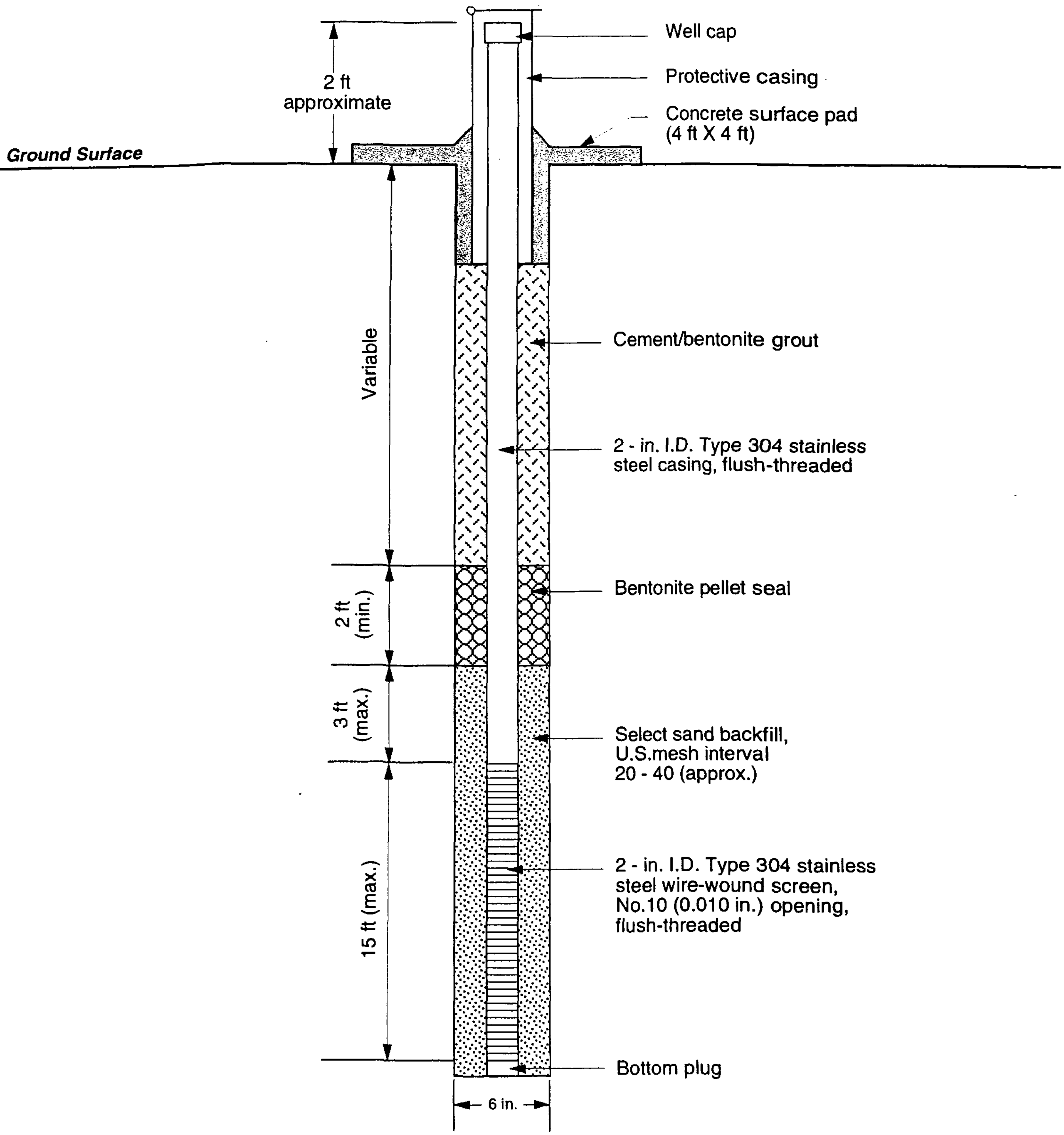
Well No.	Volume Purged	Time	Analysis	Sample Container Vol. and Mat'l.; Preserv.	Temp. (°F/C)	Spec. Conduct μ mhos/cm	Disolved Oxygen mg/L	pH

GROUNDWATER
SERVICES, INC.

EXAMPLE WATER SAMPLING LOG

QAPP for Work Plan for DNAPL Characterization and Remediation Study
Sauget Area 1
Sauget, Illinois

FIGURE
4.4



GROUNDWATER SERVICES, INC.

TYPICAL PIEZOMETER CONSTRUCTION DETAILS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1
Sauget, Illinois

FIGURE

4.5

5

5.0 CUSTODY PROCEDURES

In order to generate legally defensible analytical data, sample custody procedures will be implemented for handling environmental samples and associated records during sample collection, shipment, transfer, and storage. These procedures will support the authenticity of sampling data by tracing samples from the time of collection, through analysis, data generation, and report preparation.

A sample is considered to be within custody if the item is i) in one's physical possession; or ii) in one's view after being in one's physical possession; or iii) in a locked receptacle after being in one's physical possession; or iv) in a designated secure area. Procedures described below address custody during field sample collection, laboratory analysis, and file storage.

When completing written records to document sample custody, errors will be corrected by drawing a single line through the error, re-entering the correct information, and initialing and dating the correction.

5.1 Field Custody Procedures

Sample containers provided by the laboratory for this project will be shipped by common carrier or other suitable method in sealed coolers to a location designated by the GSI Project Manager. The laboratory will include a shipping form/laboratory chain-of-custody listing containers shipped and the purpose of each container. Containers will be considered in the custody of the laboratory until received by Solutia, GSI, or a designated representative. Upon receipt, the shipment will be checked to verify that all containers are intact. The containers will be maintained in the custody of the receiver in a clean, secure area until used for sample collection.

Procedures described below address custody during field sample collection, laboratory analysis, and file storage for the data collected in the Sauget Area 1 Sites DNAPL Study.

- Field sampling personnel will be personally responsible for the care and custody of the samples until transferred or properly dispatched.
- Sample bottles will be labeled with sample numbers and locations at the time of sample collection.
- Sample labels will be completed with permanent ink.

After collection, field sampling personnel will maintain sample custody in accordance with the following procedure:

1. The sample label affixed to the container will be inspected to confirm that all of the required information has been provided.
2. The sample container will be sealed in a zip-lock plastic bag, wrapped in bubble pack, and packed in a wet-ice or dry-ice cooler in a manner to minimize shifting or movement.
3. For each cooler sent to the laboratory, a triplicate chain-of-custody form will be completed (see Figures 5.1 and 5.2). Information on the chain-of-custody form and

the sample container labels will be checked against the field logbook entries and the samples will be recounted. The information contained on the chain-of-custody form will include the following:

- Site name and address or location;
- Project number;
- Date of sample collection;
- Name of sampler responsible for sample submittal;
- Identification of samples that accompany the form including
- Field ID number,
- Number of samples,
- Date/time collected,
- Sample container type, volume, preservative,
- Parameters/methods of interest,
- Data level requirement (e.g., Level IV),
- Comments about sample conditions;
- Signature of person relinquishing custody and signature of person accepting custody, plus date and time; and
- Identification of common carrier.

4. If a commercial courier service (e.g., Federal Express) transports the samples to the laboratory, the chain-of-custody form will be signed by a member of the field team, and a copy retained by the field team. The remaining two copies of the form will be sealed in a zip-type plastic bag and placed in the cooler with the samples. The cooler will be sealed with packaging tape and two custody seals signed and dated by a member of the field team. Custody seals will be placed on the exterior of the cooler over the lid and sides. Package routing documentation maintained by the courier service will serve as chain-of-custody documentation during shipment, because commercial couriers do not sign chain-of-custody forms.
5. If samples are picked up by a laboratory representative, a member of the field team will sign the chain-of-custody record indicating that the samples have been transferred to the lab courier. The lab courier will also sign the form, indicating that the samples have been transferred to his or her custody. One copy of the chain-of-custody form will be retained by the field team and the remaining two copies will be sealed in a zip-type plastic bag and placed in the cooler chest with the samples.

5.2 Laboratory Custody Procedures

For the Sauget Area 1 Sites DNAPL Study, normal laboratory custody procedures will be implemented. Samples received and logged into the laboratory will remain in the custody of STL Savannah or PTS Labs personnel at the laboratory until disposal.

5.2.1 Sample Receipt and Inspection

Upon arrival at the laboratory, samples will immediately be taken to the sample receiving area and logged into the laboratory sample registry in which the date and time of sample receipt will be recorded. An example sample registry page for STL Savannah is shown on Figure 5.3. The shipping container will be opened immediately and the temperature of the shipping container measured and documented on the Laboratory Task Order (see Figure 5.4).

Shipping containers having custody seals will be inspected for integrity upon arrival at the laboratory. The appropriate space on the chain-of-custody (i.e., "custody intact") will be checked "Y" for yes or "N" for no. If tampering of the custody seal is apparent, the sample custodian will immediately contact the Laboratory Project Manager who will be responsible to notify the GSI Project Manager who will then communicate with the Solutia Project Manager, as needed. A Sample Custody Excursion Form (see Figure 5.5) will be filed, and any corrective action required by Solutia will be documented on the accompanying project chain-of-custody form.

Information on the chain-of-custody form will be checked against the bottle labels and then signed by the sample custodian. The sample custodian will also inspect sample containers for leakage. A multi-phase sample which has leaked will not be acceptable for analysis, because the sample integrity has been altered. Samples in plastic containers appearing to bulge or evolve gas will be treated with caution, because toxic fumes or material of an explosive nature may be present. Discrepancies between information on sample labels and information provided on the chain-of-custody form or broken/altered samples will be resolved with Solutia and the Laboratory Project Manager before the sample is assigned for analysis.

If a custody problem occurs, the sample custodian will initial the "NOTIFIED CLIENT" blank on the sample registry and immediately notify the Laboratory Project Manager. The Laboratory Project Manager will resolve custody problem as soon as practical and notify the GSI Project Manager, if necessary. After notification, an initialed note will made on the custody form which states who was notified, reason for notification, and resolution, if applicable.

5.2.2 Internal Tracking and Numbering

The sample custodian or designee will have responsibility for maintaining sample receipt logbooks, assigning a project log number to the samples, signing the chain-of-custody form, completing the Laboratory Task Order (Figure 5.4), reporting inconsistencies to the Laboratory Project Manager, and distributing samples to the laboratory sections in accordance with applicable analytical procedures. The laboratory section sample custodian is responsible for ensuring that samples are placed in storage, for monitoring conditions in sample storage areas, and maintaining records for chain-of-custody within the laboratory. The Project Manager or designee is responsible for initiating paperwork for report files and analytical worksheets and logging samples into the Laboratory Information Management System (LIMS), if applicable.

Each sample will be assigned a unique laboratory sample number at the time of log-in to facilitate tracking of samples, extracts, and digests during analysis. The laboratory sample number will be recorded on the chain-of-custody form and Sample Registry, and logged into the computerized LIMS, if applicable. Any accompanying paper work will be placed in a project file until the order is completed. The laboratory project identification number will be recorded on all containers submitted in the project shipment.

After initiating a new log-in number, the Project Manager or designee will enter electronically or otherwise record relevant sample information, as follows:

- Laboratory sample number
- Client project identification
- Date received/date due
- Matrix/sample identification
- Date and time of sample collection
- Storage location/container size/container type/preservative
- Analyses required
- Problems/special instructions

After assignment of the project identification number, samples will be labeled to identify the project number and sample designation. The samples will then be dispersed to the appropriate sample storage area. Sample storage temperature logs will be maintained for storage refrigerators or freezers to assure maintenance of proper sample temperature throughout the analyses.

For samples requiring pH adjustment, the departmental custodian will log the samples into the departmental sample registry, check and document pH on an in-lab form and ensure that appropriate pH adjustments are made.

5.2.3 Internal Laboratory Custody Transfers

An example internal laboratory chain-of-custody record and remote division custody log are shown on Figures 5.6 and 5.7. To initiate sample analysis, the analyst will retrieve the samples from the storage area at which time the sample will be scanned out of the storage area. Records of sample receipt, retrieval, dispersal, and disposal into and out of the storage area will be maintained in the LIMS, if applicable.

5.2.4 Laboratory Storage Areas

Samples and extracts will be stored in uniquely identified refrigerated storage units located in secure areas of the laboratory. Samples are logged into the various department storage areas prior to preparation, analysis, or disposal. Samples to be analyzed for volatile organic compounds (VOCs) will be segregated from other samples. Samples will be stored separately from standards.

On a daily basis, the sample custodian or appropriate designee will measure and record the temperature of each refrigerator or freezer used for sample storage. Temperature records will be reviewed on a monthly basis to note any trends or inconsistencies. For samples to be analyzed for VOCs and SVOCs, the acceptable range for sample storage is 4±2°C. The sample custodian will notify the Laboratory Project Manager of any refrigerator temperature problem which cannot be corrected by simple thermostat adjustment. A list of emergency repair numbers will be attached to the exterior of each refrigeration unit.

5.2.5 Requirements for Sample Disposal

Unless Solutia requests the Laboratory Project Manager to save unused samples, digests and extracts, these will be disposed of as soon as holding times have expired or 30 days after results are reported to Solutia.

Excess sample portions will be composited according to matrix (solids, oils, or aqueous) by the laboratory. The composited soils, sediments and other solid samples will be sub-sampled and analyzed for hazardous waste characterization: ignitability, reactivity, releasable cyanide and sulfide, corrosivity (pH), toxicity (TCLP by SW-846 Method 1311). If the composited sub-sample is hazardous by any of the hazardous waste characteristics, the composited excess sample will be disposed of by a hazardous waste contractor. If the composited sub-sample is not deemed hazardous per these tests, the composited excess material will be disposed of in an industrial/municipal landfill.

If analyses performed on composite aqueous samples meet public sewer system discharge criteria, the composite samples will be neutralized, if necessary, and discharged into the public sewer system. Tests performed on the composite samples must demonstrate that the levels of contaminants present do not exceed hazardous characteristics.

5.2.6 Inter-Laboratory Custody Transfers

Under normal circumstances, samples will be analyzed by STL Savannah in Savannah, Georgia, or PTS Geolabs in Houston, Texas. In the event of a natural disaster (e.g., a hurricane), samples to be analyzed by STL Savannah may be sent to another Severn Trent Laboratory for analyses. When samples are transferred to another laboratory in the Severn Trent network, a chain-of-custody form will be initiated at shipping time by the sample custodian. A completed and signed fax of the Interdivisional Shipping Log will be sent to the receiving division custody department. This inter-laboratory chain-of-custody form (Figure 5.7) will be sent with the samples and upon arrival at the division laboratory, laboratory custody procedures described above will be followed.

5.2.7 Data Archiving, Storage and Final Evidence File

Laboratory records will be maintained in a secure area with other associated project records. Hard copies of final reports, chain-of-custody forms, and any ancillary documentation pertinent to the project will be stored in a secured storage area. Analytical data stored in a LIMS will be maintained under a high level of data security by the use of passwords and file access/lock codes. At the end of a project, all custody forms will be returned to the laboratory project manager. Copies of custody information will be retained in the reporting laboratories' client files. Hard copies of reports, chain-of-custody forms and sample registries will be kept by the laboratory for a period of three years. Raw data and bench data files will be kept by the laboratory for a period of three years. At the end of the three year period, or earlier upon request of Solutia, STL

Savannah and PTS will transfer custody of all project files to Solutia for inclusion in the final evidence file.

5.3 Final Evidence Files

A Final Evidence File will be developed for the Sauget Area 1 Sites DNAPL Study data including the following items: reports, field notes, laboratory reports, signed chain-of-custody forms, sampling procedures, and any other pertinent documents, including, but not limited to the following items:

- Standard operating procedures
- Field notes and field logbooks
- Laboratory reports and data deliverables
- Signed chain-of-custody documentation (tags, air bills, signed forms)
- Photographs
- Drawings
- Soil boring logs
- Data validation reports
- Data assessment reports
- Project reports

These items will be stored in a cabinet at the GSI office and access limited to concerned project personnel. The Final Evidence File will be maintained at this location until the conclusion of the project. At this time, project files will be transferred to Solutia. Contents of the Final Evidence File will be offered to USEPA Region 5 prior to disposal of project files by Solutia. The GSI Project Manager will serve as the file custodian for the Sauget Area 1 Sites DNAPL Study.

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

FIGURES

Serial Number 04509

ANALYSIS REQUEST AND CHAIN OF CUSTODY RECORD

SEVERN TRENT **STL**

STL Savannah
5102 LaRoche Avenue
Savannah, GA 31404

Website: www.stl-inc.com
Phone: (912) 354-7858
Fax: (912) 352-0165

Alternate Laboratory Name/Location
Phone:
Fax:

PROJECT REFERENCE	PROJECT NO.	PROJECT LOCATION (STATE)	MATRIX TYPE	REQUIRED ANALYSIS	PAGE OF
STL (LAB) PROJECT MANAGER	P.O. NUMBER	CONTRACT NO.	COMPOSITE (C) OR GRAB (G) INDICATE; AQUEOUS (WATER); SOLID OR SEMISOLID; AIR; NONAQUEOUS LIQUID (OIL, SOLVENT,...)		STANDARD REPORT DELIVERY; DATE DUE
CLIENT (SITE) PM	CLIENT PHONE	CLIENT FAX			EXPEDITED REPORT DELIVERY (SURCHARGE); DATE DUE
CLIENT NAME	CLIENT E-MAIL				
CLIENT ADDRESS					
COMPANY CONTRACTING THIS WORK (if applicable)				PRESERVATIVE	NUMBER OF COOLERS SUBMITTED PER SHIPMENT:

SAMPLE DATE	SAMPLE TIME	SAMPLE IDENTIFICATION	MATRIX TYPE	NUMBER OF CONTAINERS SUBMITTED	REMARKS

RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RELINQUISHED BY: (SIGNATURE)	DATE	TIME
RECEIVED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME

LABORATORY USE ONLY

RECEIVED FOR LABORATORY BY: (SIGNATURE)	DATE	TIME	CUSTODY INTACT YES / NO	CUSTODY SEAL NO.	STL SAVANNAH LOG NO.	LABORATORY REMARKS

STL8240-680 (12/02)

EXAMPLE CHAIN OF CUSTODY FORM STL

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1, Sauget, Illinois

FIGURE 5.1

GROUNDWATER SERVICES, INC.

EXAMPLE CHAIN OF CUSTODY FORM PTS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1, Sauget, Illinois

FIGURE 5.2

DATE **PTS FILE#** **CHAIN OF CUSTODY RECORD** **PAGE** **OF**

COMPANY

ADDRESS

PROJECT MANAGER

PROJECT NAME PHONE NUMBER

PROJECT NUMBER FAX NUMBER

SITE LOCATION

SAMPLER SIGNATURE

PO#

SPECIAL HANDLING

24 HOURS 5 DAYS
72 HOURS NORMAL

OTHER

SAMPLE CONDITIONS

RECEIVED ON ICE YES/NO
SEALED YES/NO
OTHER YES/NO

ANALYSIS REQUEST

SAMPLE ID NUMBER	DATE	TIME	DEPTH, FT	PHYSICAL PROPERTIES PACKAGE, API RP40	MOISTURE CONTENT, ASTM D2216	POROSITY, API RP40	GRAIN DENSITY, API RP40	BULK DENSITY, API RP40	AIR PERMEABILITY, API RP40	SPECIFIC RETENTION/YIELD ASTM D425	CAPILLARY PRESSURE, ASTM D425M	SOIL pH, EPA 9045	GRAIN SIZE: DRY; 400 MESH	GRAIN SIZE: SIEVE & LASER	GRAIN SIZE: LASER; 1 MICRON	HYDRAULIC CONDUCTIVITY, EPA 9100, API RP40	TOC: WALKLEY-BLACK	HYDRAULIC CONDUCTIVITY PACKAGE	ATTERBERG LIMITS, ASTM D4318	TNRCC PROPERTIES PACKAGE					NUMBER OF SAMPLES	COMMENTS

1. RELINQUISHED BY	2. RECEIVED BY	3. RELINQUISHED BY	4. RECEIVED BY
COMPANY	COMPANY	COMPANY	COMPANY
DATE TIME	DATE TIME	DATE TIME	DATE TIME

PTS GeoLabs, Inc. • 8100 Secura Way • Santa Fe Springs, CA 90670 • Phone (562) 907-3607 • Fax (562) 907-3610
PTS GeoLabs, Inc. • 4342 W. 12th St. • Houston, TX 77055 • Phone (713) 680-2291 • Fax (713) 680-0763

SEVERN TRENT STL

SAMPLE REGISTRY

LOG NO.	TIME RECEIVED	DATE RECEIVED	DELIVERED BY	CLIENT ID	NUMBER OF COOLERS RECEIVED	INITIATE ANOMALLY? Y/N	CONTAINER TEMPERATURE CORRECT	ADDITIONAL SAMPLE INFORMATION

FCU007:03.28.01:2

SEVERN TRENT STL

COOLER RECEIPT FORM

Client:	**Project:**
STL Log #:	**Date Received:**
Sample Custodian (Signature):	

Use other side of this form to note details concerning custodial discrepancies

		YES	NO
1	Did a shipping slip (air bill, etc.) accompany the cooler shipment?		
2	Were custody seals affixed to the outside of cooler? If YES, enter the following: Seal Identification (if provided):		
3	Were custody seals unbroken and intact at the date and time of arrival?		
4	Were custody papers completed properly (ink, signed, etc.)?		
5	Chain of custody associated with cooler receipt form.		
6	Was wet ice/blue ice used? (Circle which media)		
7	Cooler temperature upon receipt:		
8	Describe type of packing in cooler (vermiculite, bubble pack, etc.).		
9	Were sampling containers supplied by SL or client? (Circle which one)		
10	Did all bottles arrive intact and were labels in good condition?		
11	Did all bottle labels agree with custody papers?		
12	Were bubbles present in VOA samples?		
13	Was the project manager notified of any custody discrepancies or excursions?		
14	Was a custody excursion form completed and a copy provided to the project manager? If so, complete No. 15.		
15	Who was contacted? By whom: Date:		

FCU013:06.07 01:3

GROUNDWATER SERVICES, INC.

EXAMPLE COOLER RECEIPT FORM

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1, Sauget, Illinois

FIGURE 5.4

SEVERN TRENT STL

ANOMALY REPORT

Date: ________ Log #: ________ Sample ID: ________ Client: ________

Dept: ___ EX ___ GE ___ LC ___ ME ___ RA ___ CU ___ SG ___ SM ___ VG ___ VM ___ AI

Analysis: ________ Reported by: ________

Anomaly:

Sample matrix is different than indicated by log-in.

Logged in as	*Best described as*	
Water	*Water*	*Non-aqueous liquid*
Soil	*Soil*	*Sludge*
Oil	*Oil*	*Product*
	Other ________	

Sample was received with inadequate preservation, and was preserved upon receipt.

Sample received in an incompatible sample container. ___ *glass* ___ *plastic* ___ *other* ________

MS/MSD failed while the LCS/LCSD passed criteria, for a drinking water parameter. Method indicates data qualification.

Target analyte(s) detected in drinking water sample. (Describe below)

Sample exhibits gross non-homogeneity. (Describe below)

Insufficient sample received for analysis.

Data qualifier needed. Discuss with DM/LM before reporting.

Grand Mean exception was utilized for Initial Calibration (specify compounds). (SW-846 Only)

Grand Mean exception was utilized for Continuing Calibration (specify compounds). (SW-846 Only)

Other ____

Custody: ***ALWAYS ATTACH A COPY OF COC WITH HIGHLIGHTED DEFICIENCY**

- Sample description discrepancy between COC & Container
- Sample container breakage
- Cooler temp >6°C or frozen
- Sample received not listed on COC
- Custody seals broken
- Incomplete COC
- Sample container partially filled
- Improperly preserved sample

Comments:

Client Notified: Yes No
Contact:

Date:

Resolution:

Route to:

Project Manager: ________________________

STL Facility. Savannah______ Mobile______ Tampa West______ Tallahassee______

FAN038:10.12.01:6

GROUNDWATER SERVICES, INC.

EXAMPLE ANOMALY REPORT

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1, Sauget, Illinois

FIGURE

5.5

GROUNDWATER SERVICES, INC.

SEVERN TRENT **STL**

STL Savannah LQM
Section 5 Revision: 0
Effective Date: 02.03.03

SAMPLE INTERNAL CUSTODY LOG

STL LOG NO.____________________

CLIENT:____________________ COURIER:____________________

COOLERS/CLIENT:____________________ TEMPERATURE____________________

GENERAL CONTAINER TYPE LIQUID	P	#	METALS CONTAINER TYPE LIQUID	P	#	VOLATILE CONTAINER TYPE LIQUID	P	#	EXTRACTION CONTAINER TYPE LIQUID	P	#
L N/M PLASTIC			500 M/M PLASTIC			40 ML VIAL			L N/M AMB GLASS		
250 AMB GLASS			250 M/M PLASTIC			**SOIL**			250 M/M AMB GLASS		
500 M/M PLASTIC			100 M/M PLASTIC			ENCORE SPLERS/25g			500 M/M AM GLASS		
500 M/M AMB GLASS			**SOIL**			ENCORE SPLERS/5g			500 M/M PLASTIC		
250 N/M PLASTIC			L W/M PLASTIC			125 AMB W/M W/SEPTA			250 M/M PLASTIC		
250 N/M PLASTIC			500 W/M PLASTIC			125 AMB W/M GLASS			**SOIL**		
250 M/M NALGENE			250 W/M PLASTIC			**AIR**			L W/M GLASS		
125 M/M AMB GLASS			**OTHER**			TEDLAR BAG			500 W/M GLASS		
100 M/M PLASTIC						SUMMA CANS			250 M/M GLASS		
DO BOTTLE						VACUUM CANS			**OTHER**		
SOIL						**TUBES**					
250 M/M NALGENE						**OTHER**					
OTHER											
						PLEASE VERIFY					
PLEASE VERIFY	4		**PLEASE VERIFY**	4		**TOTAL CONTAINERS**	4		**PLEASE VERIFY**	4	
TOTAL CONTAINERS			**TOTAL CONTAINERS**						**TOTAL CONTAINERS**		

RELINQUISHED INFORMATION:

CUSTODY INITIAL/DATE __________ CUSTODY INITIAL/DATE __________ CUSTODY INITIAL/DATE __________ CUSTODY INITIAL/DATE __________

GENERAL INITIAL/DATE __________ METALS INITIAL/DATE __________ VOLATILES INITIAL/DATE __________ EXTRACTION INITIAL/DATE __________

MISC. BOTTLES STORED IN REFRIGERATOR FOR SUBCONTRACT/REMOTE TRANSFER:

EXAMPLE SAMPLE INTERNAL CUSTODY FORM

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1, Sauget, Illinois

FIGURE **5.6**

SEVERN TRENT SERVICES

FIGURE 6

REMOTE DIVISION

SAMPLE INTERNAL CUSTODY LOG

STL FACILITY: ____________________

 # COOLERS ____________________

TEMPERATURE(S) ____________________

LOG # FOR GENERAL LAB	#	LOG # FOR METALS LAB	#	LOG # FOR VOLATILES LAB	#	LOG # FOR EXTRACTION LAB	#
PLEASE VERIFY ✓		PLEASE VERIFY ✓		PLEASE VERIFY ✓		PLEASE VERIFY ✓	
TOTAL CONTAINERS		TOTAL CONTAINERS		TOTAL CONTAINERS		TOTAL CONTAINERS	

RELINQUISHED INFORMATION:

CUSTODY INITIAL/DATE **CUSTODY** INITIAL/DATE **CUSTODY** INITIAL/DATE **CUSTODY** INITIAL/DATE

GENERAL INITIAL/DATE **METALS** INITIAL/DATE **VOLATILES** INITIAL/DATE **EXTRACTION** INITIAL/DATE

FCU027:06.19.01:2

GROUNDWATER SERVICES, INC.

EXAMPLE REMOTE DIVISION SAMPLE INTERNAL CUSTODY LOG

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Saugет Area 1, Sauget, Illinois

FIGURE 5.7

6.0 CALIBRATION PROCEDURES AND FREQUENCY

This section describes the calibration procedures and the frequency at which these procedures will be performed for both field and laboratory instruments.

6.1 Field Instrument Calibration

The only field instruments to be used for this project will be PID organic vapor analyzers. These instruments will be maintained and calibrated with sufficient frequency and in such a manner that accuracy and reproducibility of results will be consistent with the manufacturer's specifications.

Equipment will be examined prior to conducting field activities to verify proper operating condition. This will include review of the appropriate SOP and equipment maintenance schedule to ensure that required maintenance is completed. Field notes from previous sampling trips will be reviewed for notation of prior equipment problems, and to ensure that necessary repairs to have been completed.

PIDs will be calibrated and checked on a daily basis in accordance with the procedures provided in the accompanying Field Sampling plan which will include a check of the following components: i) probe and cable, ii) lamp, and iii) battery. Each instrument will also receive an annual maintenance check by a qualified technician. Instruments may require more frequent calibration due to inclement weather, high constituent concentrations, instrument handling, or other factors.

Calibrations will be documented in the field logbook and will include the date/time of calibration, name of person performing the calibration, reference standards used, temperature at which readings were taken, and the readings. Multiple readings on the one sample or standard, as well as readings on replicate samples, will likewise be documented. Internally calibrated field instruments failing to meet calibration/check-out criteria will be returned to the manufacturer for service and an alternate instrument will be used. The accuracy and traceability of reference standards used for field instrument calibration will be documented by recording the manufacturer's name and the standard lot number in the instrument calibration log book.

6.2 Laboratory Instrumentation Calibration

The laboratory will employ specific procedures for the operation and calibration of analytical instruments in order to facilitate optimum instrument performance, thereby generating data of acceptable accuracy and precision. Prior to initiating sample analysis, laboratory instruments will demonstrate acceptable performance with respect to applicable standards from the manufacturer or selected reference methods (i.e., USEPA, API, or ASTM). Appendix A of this QAPP presents SOPs to be employed by STL and PTS for calibration of laboratory instrumentation during analysis of samples collected during the DNAPL Study.

6.2.1 Storage of Standards

As soon as practical after receipt, standards will be transferred to a designated storage area in the laboratory. Volatile standards will be stored in a freezer; semi-volatile standards at room temperature; and other commercially purchased stock standards at 4°C, in a freezer, or at room temperature, as appropriate. Organic standards will be stored separately from samples. Certification sheets will be kept on file within each lab division and stored for future reference.

6.2.2 Traceability of Standards

Standards used for calibration of instrumentation used in analyzing samples for the DNAPL Study will be NIST traceable, EPA A2LA certified, or obtained from another appropriate source. Records will be maintained to verify the traceability of all standards used and will include pertinent information such as the date, analyst, compound, purity, dilution volume, etc., as appropriate. Additional details concerning the preparation and use of standards is documented in the SOPs provided in Appendix A of this QAPP.

6.2.3 Instrument Calibration

Instrument calibration protocols will meet or exceed the requirements specified in the EPA, API, or ASTM reference method employed for sample analysis. Details for calibrating gas chromatographs, mass spectrometers, inductively coupled plasma/atomic absorption spectrophotometers, and other instruments to be used in the Shell RA program are provided in Appendix A of this QAPP. Initial instrument calibration curves will be generated, verified, and routinely monitored during instrumental analyses, as required by specific SOPs. Records of calibration, repairs, or replacement will be maintained by the designated laboratory personnel performing quality control activities and filed at the location where the work is performed.

7.0 ANALYTICAL PROCEDURES

7.1 Field Analytical and Measurement Procedures

Field screening measurements of organic vapors in soil will be conducted by field personnel in accordance with procedures in the Field Sampling Plan. These measurements will be made in the field at the time of sampling.

7.2 Laboratory Analytical and Measurement Procedures

7.2.1 List of Project Target Compounds and Laboratory Detection Limits

7.2.1.1 Organic Compounds and Metals

Table 7.1 provides a cross-reference between EPA reference methods and laboratory SOPs provided in Appendix A. STL Savannah will analyze soil samples collected during the Sauget Area 1 Sites DNAPL Study as well as water samples obtained from soil cores during the treatability study for VOCs and SVOCs in accordance with USEPA SW-846 methods. NAPL samples will be analyzed by STL Savannah for VOCs, SVOCs, organochlorine pesticides, chlorinated herbicides, PCBs, dioxins and furans, and metals in accordance with USEPA SW-846 methods. Analytical procedures and project-specific laboratory reporting limits for organic compounds an metals in soil, water, and NAPL as analyzed by USEPA SW-846 methods are provided on Tables 1.1, 1.2, and 1.3, respectively. Laboratory reporting limits for SW-846 methods have been experimentally determined in accordance with FR vol. 49, no. 209, page 198-199 and SOPs CA90 and CA92 (see Appendix A).

Detection limits for the Sauget Area 1 Sites DNAPL Study will be laboratory Reporting Limits (RLs) corresponding to three to five times the method detection limit (MDL). The laboratory will report COC concentrations at or below the RLs described in this QAPP, unless the specified detection limits are not obtainable by the laboratory due to high parameter concentrations requiring sample dilution or matrix interferences. The laboratory will report COC concentrations less than the RL but greater than the MDL as estimated and will flag such results as estimated values in accordance with the laboratory data reduction procedures specified in Section 9 of this QAPP.

STL Savannah has previously conducted a baseline detection limit study for all methods per USEPA CLP guidelines, and records of the study are maintained at the laboratory. Results of the study are periodically updated and/or revised when changes in instrumentation or methods occur within the laboratory. This study is intended to establish, in accordance with accepted regulatory procedures, the baseline (lowest possible) method detection limits (MDLs) and instrument detection limits (IDLs) obtainable by the laboratory. STL Savannah maintains on file the results of the most recent detection limit study for project specific COCs.

Samples to be analyzed for volatile organics will be screened in the laboratory as described in the VOA SOP. Samples will be analyzed either as low or medium level concentration samples or as a series of dilutions in order to cover the expected concentration range of the site-specific compounds of interest. If necessary, soil or NAPL samples to be analyzed for SVOCs will be subjected to gel permeation chromatography cleanup and/or other column chromatography cleanup.

7.2.1.2 Physical Properties

PTS in Houston, Texas, will analyze core samples and soil samples for physical properties in accordance with laboratory SOPs prepared and reviewed for consistency with API and ASTM reference methods (see Table 7.1). Laboratory reporting limits for physical properties (see Table 1.4) have been experimentally determined in accordance with the applicable API or ASTM reference method and corresponding laboratory SOP (see Appendix A).

7.2.2 List of Associated QC Samples

As summarized on Table 3.1, each laboratory SOP includes a QC section addressing minimum QC requirements for the analysis of specific analyte groups (see Appendix A).

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

TABLES

GROUNDWATER SERVICES, INC.

TABLE 7.1
EPA, API and ASTM REFERENCE METHODS AND CORRESPONDING LABORATORY STANDARD OPERATING PROCEDURES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Matrix	Laboratory Analytes	Reference Method	Laboratory SOP
Soil	Volatile Organics	Extraction: 5035 Analysis: 8260B	Extraction and Analysis: VM20:11.12.99:4
	Semi-Volatile Organics	Extraction: 3510/3520/3550/3640 Analysis: 8270C	Extraction and Analysis: SM05:08.27.02:7
	Total Organic Carbon	Analysis: EPA-CE (Walkely-Black)	Analysis: BA05:08 27 02:3
Water	Volatile Organics	Analysis: 8260B	Analysis: VM20:11.12.99:4
	Semi-Volatile Organics	Extraction: 3510/3520/3550/3640 Analysis: 8270C	Extraction and Analysis: SM05:08.27.02:7
NAPL	Metals	Extraction: 3050B Analysis: 6010	Extraction: ME51:03.06.01:2 Analysis: ME70:03.07.01:7
	Mercury	Analysis: 7471A	Analysis: ME28:12.15.00:2
	Pesticides	Extraction: 3580 Analysis: 8081	Extraction: EX42:07.06.98:0 Analysis: SG45:01.30.02:7
	Herbicides	Extraction: 3580 Analysis: 8151	Extraction: EX42:07.06.98:0 Analysis: SG65:11.05.02:5
	PCBs	Extraction: 3580 Analysis: 8082	Extraction: EX42:07.06.98:0 Analysis: SG45:01.30.02:7
	Dioxins and Furans	Analysis: 8280A/8290	Analysis: SM10:02.06.02:5
Soil Core	Free Product Mobility: Centrifuge Method Fluid Saturation: Dean Stark Method Total Porosity Grain Density Bulk Density Viscosity Surface and Interfacial Tension Particle Size Air-Filled Porosity	API RP 40 / ASTM D425M API RP 40 API RP 40 API RP 40 API RP 40 / D2937-94 ASTM D445 ASTM D971 ASTM D422-63 API RP 40	NA NA NA NA NA NA NA NA NA

Notes:
1. Tables 1.1, 1.2, 1.3, and 1.4 provide complete list of analytes.
2. Laboratory SOPs are provided in Appendix A.
3. Methods for physical properties analysis to be performed by PTS Geolabs are provided in Appendix A.
4. NAPL samples are analyzed by solid waste methods using waste dilution (EPA 3580) for the extract preparation.
5. NA = No SOP number assigned to this method.

8.0 INTERNAL QUALITY CONTROL CHECKS

8.1 Field QC Checks

Field QC samples will be collected and analyzed in order to i) evaluate field precision and accuracy, and ii) facilitate validation of sample results. Field sampling precision and accuracy will be assessed through the collection and laboratory analysis of field replicates and field blanks. Samples will be collected per applicable procedures provided in the Field Sampling Plan.

Data from field QC samples will be examined to determine if any problems are evident for specific media or with laboratory procedures. The Contractor QA Manager will advise the Contractor Project Manager of the problems encountered so that the appropriate corrective action can be taken. Procedures for communicating corrective actions are described in Section 13 of this QAPP.

8.1.1 Blank Samples

8.1.1.1 Equipment Rinsate Blanks

Equipment rinsate blanks will be collected to verify the efficacy of cleaning procedures for sampling equipment. After use and decontamination, rinsate blanks will be collected by i) placing laboratory-grade (organic-free/de-ionized or distilled) water in contact with the field sampling apparatus (e.g., coring device, spoon, bowl, bailer, or pump tubing); ii) collecting the rinsate in method-specified sample containers with appropriate preservatives; and iii) analyzing for the VOCs and SVOCs. For this project, rinsate blanks will be collected at a frequency of one equipment blank for every 10 samples (10%) per sample matrix and type of equipment; however, no more than one equipment rinsate blank per day per sample matrix and type of equipment will be collected. Equipment rinsate blanks will be appropriately labeled and documented in field records. Blanks will be stored, transported, and analyzed with associated samples. No equipment rinsate blanks will be collected or analyzed if dedicated sampling equipment is used.

8.1.1.2 Trip Blanks

The effectiveness of sample handling techniques will be evaluated by submitting preserved trip blank samples for laboratory analysis. Trip blanks will consist of a pair of 40-mL VOA vials with Teflon™ lined septa, filled in the laboratory (or organization providing the sample containers) with laboratory-grade (organic-free/de-ionized or distilled) water. The unopened trip blanks will accompany the VOC sample bottles to the sampling site and back to the laboratory in the same shipping cooler. Proper labeling and documentation will be completed for trip blanks. Trip blanks will be prepared and analyzed with other samples being analyzed for VOCs at a minimum frequency of one per day when sampling soil or water only (i.e., no trip blanks will be required if NAPL is the only medium sampled on a particular day).

8.1.2 QC Check Samples

The precision of field sample collection techniques will be evaluated by collecting and analyzing field duplicates. Duplicate samples will be defined as those samples collected simultaneously from the same source under identical conditions into separate but identical containers, and preserved, stored, transported and analyzed in the same manner. Thus, to prepare a duplicate, an aliquot will be collected from a sample source (i.e., soil, water, and NAPL) and divided equally into two separate but identical sample containers. Each duplicate will be identically preserved, stored, transported and analyzed. Field duplicates will be given a different identification number to disguise the source of the sample from the laboratory. Field replicates will be analyzed by the same laboratory analyzing investigative samples.

During the course of the DNAPL Study, duplicates will be collected at a frequency of one duplicate for every 10 samples (10%) for each matrix (i.e., soil, water, and NAPL). Field duplicates will be analyzed for VOCs and SVOCs only.

8.1.3 Field Instrument QC Check Samples

Given that the soil vapor concentrations measured by PID will be used for screening purposes only, no field instrument QC check samples will be required.

8.2 Laboratory QC Checks

8.2.1 Analysis of Soil, Water, and NAPL for COCs

STL Savannah will implement a QA/QC program to ensure the reliability and validity of analyses performed in the laboratory. Analytical procedures will be documented in writing as SOPs, each including a section addressing minimum QC requirements for the procedure. Internal quality control checks differ slightly for individual procedures, but in general QC requirements will include the following:

- Method blanks
- Instrument blanks
- Matrix spikes/matrix spike duplicates
- Surrogate spikes
- Laboratory duplicates
- Laboratory control standards
- Surrogate spikes
- Internal standard spikes
- Mass spectral tuning

QC sample results will be properly recorded and included in the analytical data package. The data package will contain sufficient QC information to allow reconstruction and evaluation of the laboratory QC process by an independent data reviewer.

Data generated in the laboratory will be properly recorded and compiled into a deliverable package containing sufficient QC information for comparison to relevant criteria. Samples analyzed in non-conformance with the QC criteria will be re-analyzed by the laboratory if sufficient volume is available. The sample volumes listed on Table 4.1 generally provide sufficient volumes and/or weights of sample for re-analysis, if required.

Laboratory Internal Quality Control Program: Data quality objectives for internal laboratory control checks will be consistent with USEPA precision and accuracy criteria specified for selected analytical methods. STL Savannah will continue to demonstrate an ability to produce acceptable results using the methods selected through the generation of acceptable QC data. Analytical data will be evaluated by STL Savannah prior to submittal based on internal reviews of the QC data. Analytical quality control checks will be performed in the laboratory. These procedures will be based upon USEPA reference methods and generally accepted standards of good laboratory practice. Key components of the laboratory Analytical Quality Control Program include the following quality control practices and considerations:

- Designation of a Laboratory QA Manager to implement the laboratory QA/QC program;
- Adherence to specified laboratory sample acceptance procedures to maintain proper handling, processing, and storage of submitted samples;
- Use of the computerized laboratory data management system to record, document, and assimilate pertinent technical and administrative data;
- Use of USEPA reference methods and recommended instrumentation;
- Adherence to mandatory procedures for operation, calibration, and maintenance of laboratory and field instrumentation;
- Use of proper laboratory measuring equipment, glassware, water, chemical reagents, industrial gases;
- Constant surveillance and documentation of acceptable analytical method accuracy and precision through initial analytical method performance evaluations;
- Use of continuous surrogate spike recovery evaluations, where appropriate, to maintain acceptable method performance;
- Use of systematic method blank evaluations to identify analytical system interferences and background contamination levels;
- Adherence to proper laboratory documentation measures to maintain the complete integrity and legal validity of all laboratory analyses;
- Use of voluntary intra-laboratory performance evaluations to internally assess and evaluate analytical performance; and
- Participation in laboratory certifications, audits, and approval programs.

Analytical Data Quality: The principle criteria for validating data quality will be the continuous monitoring of acceptable analytical accuracy, precision, and overall method performance, through systematic analyses of quality control samples. STL Savannah will conduct both initial and continuous analytical method performance evaluations to ensure that all generated analytical data meet applicable QC and method performance criteria. Each analytical method commonly used in the laboratory will utilize specific quality control procedures to continually monitor acceptable analytical method accuracy and precision. These specific quality control procedures are detailed in the analytical methods SOPs based upon USEPA reference methods. QC criteria for internal standards for analysis of VOCs and SVOCs are provided on Table 8.1.

8.2.2 Analysis of Soil Properties

PTS will implement a QA/QC program to ensure the reliability and validity of analyses performed in the laboratory. Analytical procedures will be documented in writing as SOPs, including minimum requirements for internal QC checks if any are specified by the corresponding API or ASTM reference method. QC sample results will be properly recorded and included in the analytical data package. The data package will contain sufficient QC information to allow reconstruction and evaluation of the laboratory QC process by an independent data reviewer.

Data generated in the laboratory will be properly recorded and compiled into a deliverables package containing sufficient QC information for comparison to relevant criteria. Samples analyzed in non-conformance with the QC criteria will be re-analyzed by the laboratory if sufficient volume is available.

Data quality objectives for internal laboratory control checks will be consistent with API and ASTM precision and accuracy criteria specified for selected analytical methods. PTS will continue to demonstrate an ability to produce acceptable results using the methods selected through the generation of acceptable QC data. Analytical data will be evaluated by PTS prior to submittal based on internal reviews of the QC data. Analytical quality control checks will be performed in the laboratory be based upon API and ASTM reference methods and generally accepted standards of good laboratory practice. Key components of the laboratory Analytical Quality Control Program include the following quality control practices and considerations:

- Designation of a Laboratory QA Manager to implement the laboratory QA/QC program;
- Adherence to specified laboratory sample acceptance procedures to maintain proper handling, processing, and storage of submitted samples;
- Use of the computerized laboratory data management system to record, document, and assimilate pertinent technical and administrative data;
- Use of API and ASTM analytical methods and instrumentation;
- Adherence to mandatory procedures for operation, calibration, and maintenance of instrumentation;

- Use of proper laboratory measuring equipment, glassware, water, chemical reagents, industrial gases;
- Constant surveillance and documentation of acceptable analytical method accuracy and precision through initial analytical method performance evaluations;
- Adherence to proper laboratory documentation measures to maintain the complete integrity and legal validity of all laboratory analyses;

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

TABLES

TABLE 8.1
LABORATORY CONTROL LIMITS FOR INTERNAL STANDARDS: VOLATILE AND SEMI-VOLATILE ORGANICS

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Parameter	EPA SW-846 Reference Method	Laboratory Control Limits Relative to Calibration Standard	
		Peak Area Counts	**Retention Time**
Volatile Organics			
1,2-Dichloroethane-d4	8260B	50% to 200%	+/- 0.5 minutes
1,4-Difluorobenzene	8260B	50% to 200%	+/- 0.5 minutes
Chlorobenzene-d5	8260B	50% to 200%	+/- 0.5 minutes
Semi-Volatile Organics			
1,4-Dichlorobenzene-d4	8270C	50% to 200%	+/- 0.5 minutes
Naphthalene-d8	8270C	50% to 200%	+/- 0.5 minutes
Acenaphthene-d10	8270C	50% to 200%	+/- 0.5 minutes
Phenanthrene-d10	8270C	50% to 200%	+/- 0.5 minutes
Chrysene-d12	8270C	50% to 200%	+/- 0.5 minutes
Perylene-d12	8270C	50% to 200%	+/- 0.5 minutes

Notes:
1. Control limits based upon data provided by STL.
2. Laboratory procedures will be conducted in accordance with the EPA reference methods shown above.
3. See Appendix A of this QAPP for laboratory SOPs.
4. Liquid samples include all samples having a solids content of less than 1%, i.e., groundwater, surface water, river water, stream water.
5. Solid samples include all samples having a solids content of greater than 1%, i.e., soil, sediment, sludge, oil, and NAPL.

9

9.0 DATA REDUCTION, VALIDATION, AND REPORTING

Data generated during field and laboratory analyses will be reduced and validated prior to reporting. No data shall be disseminated by the field crew or the laboratories until subjected to the reduction and validation procedures described below. For both field and laboratory data recording and reduction, errors will be corrected by drawing a single line through the error, re-entering the correct information, and initialing and dating the correction.

9.1 Data Reduction

9.1.1 Field Data Reduction Procedures

Field measurements will be taken directly from PID organic vapor analyzers which are direct reading instruments requiring no data reduction; therefore, data from these instruments will be written into field log books immediately after measurements are taken.

9.1.2 Laboratory Data Reduction Procedures

In order to convert raw data from instrument reading to reportable results, raw data will be reduced to reportable values by instrument hardware and software or by other manual procedures suggested in the applicable reference method. Reduction of laboratory measurements and laboratory reporting of analytical parameters will be conducted in accordance with the procedures specified for each USEPA, API, or ASTM analytical method. Data reduction and recordkeeping activities of the primary analyst will be as follows:

- ***General Data Reduction:*** All methods employed for analysis of samples collected during the DNAPL Study will involve certain data reduction procedures following established laboratory QA/AC protocol. The analyst will record and maintain accurate laboratory records and computer files to include sample identification, weights or volumes, dilution factors, analysis date and method, and analyst initials. Proper instrument and method calibrations will be performed and verified. The analyst will confirm results of the analytical sequence or batch, including QA/QC verification. After converting raw data to final form by following proper procedures for calculations, rounding, and significant figures, sample results will be manually transcribed or automatically transferred from the instrument report to the results data sheet. Equations for data reduction are provided in the laboratory SOPs contained in Appendix A of this QAPP. Internal chain-of-custody records will be maintained as described in Section 5 of this QAPP. The laboratory will flag analytical results in order to note the conditions listed below:
  - U = Analyte was analyzed for but not detected.
  - J = Results are estimated owing to mass spectral data indicating the presence of a compound meeting applicable identification criteria, but quantitated at less than the MQL and greater than the MDL.
  - B = Analyte detected in corresponding method or laboratory blank.

- X = Results are flagged for a reason other than specified above as noted by the laboratory.

- ***Sample Preparation:*** Preparation analysts will record accurate data used in final calculations. Such data will be maintained in extraction and digest logbooks, bench sheets, and chemist's notebooks containing sample weights or volume, final extract volumes, surrogate and spike amounts, and standard reference numbers.
- ***Soil Properties Analyses:*** Duties of the soil properties analyst will include recording results from direct-reading or automated instruments onto a data sheet. The analyst will be responsible for transcribing, as necessary, results for selected soil properties parameters to spreadsheets for data reduction. Final results will be recorded on a data sheet and then entered into the Laboratory Information Management System (LIMS), as applicable.
- ***Instrument Analyses:*** Instrument analysts will verify calculations, analyte identifications, related QA/QC calculations, and sample results. Calculations will include surrogate spike recoveries, laboratory control sample (LCS) recoveries results of sample duplicates and matrix spikes, and results for method and matrix-specific blanks. Lab results will be recorded by the analyst on a data sheet and the associated QA/QC data sheet. Computer or integrator reduction will be employed for the analysis of volatile and semi-volatile organics by GS/MS. Instrumentation will generate a quantitation report and sample results will be calculated by computer integration, spreadsheet, or manual calculation. Positive sample results will be transcribed by the analyst to the sample results sheet and QC data entered into a QA/QC summary spreadsheet.
- ***Record Keeping:*** Bench sheets for sample extraction, digestion, and soil properties will be maintained in bound notebooks. Chromatographic documentation and data record will include sample preparation logs, extraction logs, bench sheets, instrument logs, instrument tune reports, quantitation reports, and instrument printouts. Run logs will be maintained for instrument analyses to document injection of each standard, quality control sample, and client sample. Equipment maintenance logs will be employed to document maintenance activities as discussed in Section 11 of this QAPP. Completion of chain-of-custody forms is discussed in Section 5 of this QAPP. Unused areas of the daily bench sheets and instrument logs will be crossed out, initialed and dated by the corresponding analyst or technician.

9.2 Data Validation

Data validation procedures will be performed for both field and laboratory operations as described below.

9.2.1 Procedures Used to Validate Field Data

The field data package, including field records and measurements acquired by the sampling team personnel, will be reviewed by the GSI QA Manager, as follows:

- Field records and sampling logs for soil and NAPL will be reviewed for completeness and accuracy.

- Sampling records and chain-of-custody forms will be reviewed to verify that samples, field duplicates, equipment rinsate blanks, and trip blanks were collected at the frequency specified in the QAPP and were properly prepared, preserved, and submitted to the laboratory.
- PID field records will be reviewed for documentation of proper calibration and maintenance.
- Chain-of-custody forms will be reviewed for proper completion, signatures of field personnel and the laboratory sample custodian, and dates.

9.2.2 Procedures Used to Validate Laboratory Data

Data production will begin with the generation of data results by the analyst and continue through a multi-level review and validation process. Each step in the review process will be performed to assure the integrity and validity of the data generated by the laboratories. Data will be sequentially passed on to the peer review analyst of the staff chemist, the department supervisor, and finally the data entry personnel. The laboratory report will be reviewed by the Laboratory QA Manager assigned to the project and then will be certified by the laboratory manager or designee. Each step in the review process will be performed to assure the integrity and validity of the date generated by the laboratories, as follows:

Quality control data (e.g., laboratory duplicates, surrogates, matrix spikes, and matrix spike duplicates) will be compared to method acceptance criteria. Data considered to be acceptable will be entered into the laboratory computer system. Data summaries will be sent to the Laboratory QA Manager for review. If approved, data will be logged into the project database. Unacceptable data will be appropriately qualified in the project report. Case narratives will be prepared to include information concerning data falling outside acceptance limits, and any other anomalous conditions encountered during sample analysis. Data will be issued after approval by the Laboratory QA Manager.

9.3 Data Reporting

9.3.1 Field Data Reporting

Field data reporting comprises a tabulation of the results of measurements made in the field (i.e., PID readings and geologic logs).

9.3.2 Laboratory Data Reporting

9.3.2.1 STL Savannah

A LIMS will be utilized for generation of laboratory data reports. After data have been entered and verified as described in Section 9.2 above, a draft report will be generated for review by the Laboratory QA Manager. CLP-like (i.e., Level IV) deliverables will be provided for those analyses where such information is available (i.e., metals, volatile organics, and semi-volatile organics). Laboratory data reports will consist of sample results plus the QA/QC data specified below. The following are general requirements for each sample analyzed by the laboratory:

- The results of each analysis;
- The list of the COCs;
- The method of analysis and the detection limit for each analyte;
- Dates of sample collection, receipt, preparation, and analysis;
- Copy of the chain-of-custody forms signed by the sample custodian;
- A narrative summarizing any QA/QC non-conformances and the corrective action taken; and
- A list relating laboratory ID to sample ID.

The list below describes the information to be provided for analysis of VOCs and SVOC by GC/MS, as applicable:

- Evaluation of holding time, sample preservation, and percent solids;
- Dilutions;
- Results of bromofluorobenzene or decafluorotriphenylphosphine GC/MS tuning;
- Results of initial and continuing calibration;
- Results of blank analyses;
- Results of surrogates spikes, the expected value, control limits, and percent recovery;
- Results of matrix spike/matrix spike duplicate, control limits, expected value, RPD, and percent recovery;
- Results for laboratory control samples, expected value, control limits, and percent recovery;
- Results of internal standards;
- Compound identification, quantification, and detection limits; and
- Results of laboratory duplicates.

The list below describes the information to be provided for analysis of organochlorine pesticides; chlorinated herbicides; and PCBs; as applicable to the specific SOP and reference method:

- Evaluation of holding time, sample preservation, and percent solids;
- Dilutions;
- Evaluation of GC performance;
- Results of initial and continuing calibration;
- Results of blank analyses;
- Results of surrogates spikes, the expected value, control limits, and percent recovery;
- Results of matrix spike/matrix spike duplicate, control limits, expected value, RPD, and percent recovery;
- Results for laboratory control samples, expected value, control limits, and percent recovery;
- Results of internal standards;
- Compound identification, quantification, confirmation, and detection limits; and
- Results of laboratory duplicates.

The list below describes the information to be provided for analysis of dioxins and furans, as applicable to the specific SOP and reference method:

- Evaluation of holding time, sample preservation, and percent solids;
- Dilutions;
- Results of GC/MS tuning;
- Column performance check standard analysis;
- Results of initial and continuing calibration;
- Results of blank analyses;
- Results of recovery standards;
- Results of matrix spike/matrix spike duplicate, control limits, expected value, RPD, and percent recovery;
- Results for laboratory control samples, expected value, control limits, and percent recovery;
- Results of internal standards;
- Compound identification, quantification, confirmation, and detection limits; and
- Results of laboratory duplicates.

The list below describes the information to be provided for analysis of metals and TOC; as applicable to the specific SOP and reference method:

- Evaluation of holding time, sample preservation, and percent solids;
- Results of initial and continuing calibration;
- Results of blank analyses;
- ICP interference check sample analysis:
- Results of laboratory duplicates and spike duplicates, expected values, control limits, and percent recoveries;
- ICP serial dilution analysis;
- Results of matrix spike/matrix spike duplicate, control limits, expected value, RPD, and percent recovery;
- Results for laboratory control samples, expected value, control limits, and percent recovery; and
- Analyte quantitation and detection limits.

The laboratory will keep on file, for a period of three years, the following information:

- Sequential measurements readout records,
- Digestion logs,
- Percent solids raw data,
- Raw data calculation worksheets,
- GC/MS tuning and mass calculations sheets,
- Sample chromatograms,
- Mass spectra data for each sample, and
- Any other data that is associated with the samples analyzed.

After the Laboratory QA Manager has determined that the report summaries and case narratives meet project requirements, data will be compiled into a CLP-like (i.e., Level IV) data package. In addition to the record of chain-of-custody, the report format will include the following:

- Case narrative:
  1. Date issued
  2. Laboratory analyses performed
  3. Deviations from intended analytical strategy
  4. Laboratory batch number
  5. Numbers of samples and respective matrices
  6. Quality control procedures utilized and references to the acceptance criteria
  7. Project name and number
  8. Condition of samples 'as-received'
  9. Whether sample holding times were met
  10. Discussion of technical problems or other observations which may have created analytical difficulties
  11. Discussion of any laboratory quality control checks which failed to meet project criteria
  12. Signature of the Laboratory QA Manager

- Chemistry Data Package
  1. Case narrative for each analyzed batch of samples
  2. Summary page indicating dates of analyses for samples and laboratory quality control checks
  3. Cross referencing of laboratory sample to project sample identification numbers
  4. Data qualifiers to be used should be adequately described
  5. Sample preparation and analyses for samples
  6. Sample results
  7. Raw data for sample results and laboratory quality control samples
  8. Results of (dated) initial and continuing calibration checks, and GC/MS tuning results
  9. Matrix spike and matrix spike duplicate recoveries, laboratory control samples, method blank results, calibration check compounds, and system performance check compound results
  10. Labeled (and dated) chromatograms/spectra of sample results and laboratory quality control checks
  11. Results of tentatively identified compounds
  12. Copies of run logs and extraction logs

9.3.2.2 PTS

After data have been entered and verified as described in Section 9.2 above, a draft report will be generated for review by the Laboratory QA Manager. Laboratory data reports will consist of sample results plus the QA/QC specified in the laboratory SOP and API or ASTM reference method.

9.4 Third-Party Data Validation

ECS Environmental Chemistry Services, located in Houston, Texas, will conduct an independent data validation of 100% of the soil, water, and NAPL data generated by STL Savannah during analysis of VOCs, SVOCs, pesticides, herbicides, PCBs, dioxin and metals (including mercury). Data packages will receive a completion check to ensure that the deliverable requirements specified for the project have been satisfied. Minimum requirements will be as follows:

- Chain-of-custody documentation associated with samples.
- A cover sheet listing samples included in the sample data group and a cross-reference between field and laboratory sample numbers.
- A case narrative describing any analytical problems encountered during analysis of the sample data group.
- Tables summarizing analytical results with reporting limits, identification, and quantification of each parameter.
- Analytical results of quality control samples (i.e., field and laboratory blanks, initial and continuing calibration verifications, spikes, duplicates, surrogates, laboratory control samples, ICP interference check samples, chromatograms, and mass spectral data).
- Raw data printouts identifying dates of preparation and analysis, analyst, parameters analyzed, calibration curves, calibration verifications, method blanks, sample dilutions, spiking levels, and preparation and run logs.

In order to qualify data for use in the DNAPL Study, a full data validation will be performed on all quality control data associated with a particular sample. After a sample has been validated each analyte will be identified as one of the following:

- Acceptable for use without restriction
- Qualified as an estimated value with a "J"
- Qualified as not detected with a "UJ"
- Rejected as unusable for the intended use with an "R"

Note that if one of the qualifiers listed above is assigned by the independent data validator, that qualifier will replace the flag assigned by the laboratory.

9.2.2.3 Data Validation for Volatile and Semi-Volatile Organic Compounds

Volatile and semi-volatile organic data will be validated in accordance with the procedures described in USEPA, *National Functional Guidelines for Organic Data Review, Multi-Media, Multi-Concentration* (OLM0.1.0, 1991 Organic Guidelines) with reference to the numerical DQO criteria in this QAPP. A full validation of volatile and semi-volatile organic data will involve a review of the following:

- Holding Times
- GC/MS Instrument Performance
- Initial Calibration
- Continuing Calibration
- Blanks

- Surrogates
- Matrix Spike/Matrix Spike Duplicates
- Internal Standards
- Target Compound Identification
- Compound Quantitation and Required Quantitation Limits
- Field Duplicates
- Overall Assessment of Data

9.2.2.4 Data Validation for Other Analyses

Data for analyses not addressed by the EPA CLP (i.e., total organic carbon and soil TOC) will be validated by comparison to the numerical DQO criteria in this QAPP. Validation of these data will involve a review of the following:

- Holding Times
- Calibration
- Laboratory Control Samples
- Duplicates
- Spike Samples, if applicable
- Sample Result Verification
- Field Duplicates
- Overall Assessment of Data

10.0 PERFORMANCE AND SYSTEM AUDITS

Performance and system audits will be conducted to verify that sampling and analysis are performed in accordance with applicable SOPs specified for field and laboratory activities in the Field Sampling Plan and Appendix A of this QAPP. The audits of field and laboratory activities include two independent components: internal and external audits.

10.1 Field Performance and System Audits

10.1.1 Internal Field Audits

10.1.1.1 Internal Field Audit Responsibilities

Internal audits of field activities, including sampling and field measurements, will be conducted by the GSI Project Manager or a designated alternate. Additional team members or Solutia personnel may also be present during various phases of the audits. These audits will be conducted to evaluate performance, verify that procedures are followed, and correct deficiencies in the execution of field procedures.

10.1.1.2 Internal Field Audit Frequency

An internal field audit will be conducted at least once at the beginning of the site sample collection activities to verify that established procedures are being followed.

10.1.1.3 Internal Field Audit Procedures

To verify compliance with established procedures and implementation of appropriate QA procedures, internal audits will involve the review and examination of the following: i) field measurement and sampling records, ii) instrument operation and calibration records, iii) sample collection documentation, iv) sample handling and packaging procedures, and v) chain-of-custody procedures. Results of field performance audits will be documented on the field audit checklist (see Table 10.1). If the first audit reveals significant deficiencies, one or more follow-up audits will be conducted to verify that QA procedures are maintained throughout the Sauget Area 1 Sites DNAPL Study.

10.1.2 External Field Audits

10.1.2.1 External Field Audit Responsibilities

External field audits may be conducted by the U.S. EPA Region 5 Project Coordinator.

10.1.2.2 External Field Audit Frequency

External field audits may be conducted at any time during the field operations. These audits may be scheduled or non-scheduled, and will be performed at the discretion of the U.S EPA Region 5 Project Coordinator.

10.1.2.3 External Field Audit Process

To verify compliance with established procedures and implementation of appropriate QA procedures, external audits will involve the review and examination of the following: i) field measurement and sampling records, ii) instrument operation and calibration records, iii) sample collection documentation, iv) sample handling and packaging procedures, and v) chain-of-custody procedures. If the first audit reveals significant deficiencies, one or more follow-up audits may be conducted to verify that QA procedures are maintained throughout the Sauget Area 1 Sites DNAPL Study.

10.2 Laboratory Performance and System Audits

10.2.1 Internal Laboratory Audits

10.2.1.1 Internal Laboratory Audit Responsibilities

Internal system and performance audits at STL Savannah and PTS will be the responsibility of the respective Laboratory QA Managers.

10.2.1.2 Internal Laboratory Audit Frequency

The internal laboratory system audit will be conducted on an annual basis, and the internal lab performance audit on a quarterly basis.

10.2.1.3 Internal Laboratory Audit Procedures

Performance and systems audits for sampling and analysis operations will include on-site review of laboratory quality assurance systems and on-site review of equipment for calibration and measurement techniques.

10.2.2 External Laboratory Audits

10.2.2.1 External Laboratory Audit Responsibilities

One or more external laboratory audits may be conducted by the U.S. EPA Region 5 Project Coordinator.

10.2.2.2 External Laboratory Audit Frequency

External laboratory audits will be conducted at the discretion of the U.S. EPA Region 5 Project Coordinator.

10.2.2.3 Overview of the External Laboratory Audit Process

External lab audits will include, but not be limited to, review of laboratory analytical procedures, laboratory on-site audits, and/or submission of performance evaluation samples to the laboratory for analysis.

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

TABLES

TABLE 10.1
EXAMPLE FIELD AUDIT CHECKLIST

QAPP for Workplan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

Audited by: ______________________ Date: ____________________

Personnel On-site: ____

____

Field Activities: ____

____

Applicable SOPs: ____

____

Requirement	Requirements Satisfied?	
	Yes	No
1.0 DOCUMENTATION		
1.1 Facility Investigation Plan on site		
1.1 Quality Assurance Project Plan on site		
1.1 Health and Safety Plan (HASP) on site		
2.0 HASP IMPLEMENTATION		
2.1 Work areas secure		
2.2 Appropriate personal protective equipment (PPE) in use		
2.3 Appropriate air monitoring being conducted		
3.0 FIELD ACTIVITIES		
3.1 Soil borings/monitoring wells installed per applicable SOPs		
3.2 Sample collection, handling, and packaging per applicable SOPs		
3.3 Sufficient number and type of QC samples collected and submitted for analysis		
3.4 Appropriate decontamination protocol observed		
3.5 Field sampling records completed properly		
3.6 Field instrument operating records completed properly		
3.7 Chain-of-custody forms completed per applicable SOP		
3.8 Custody procedures completed per applicable SOP		
3.9 Field procedures audited for each media (soil, NAPL, Core)		

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11.0 PREVENTIVE MAINTENANCE

11.1 Field Instrument Preventive Maintenance

PID organic vapor analyzers are the only field instruments to be used for the Sauget Area 1 Sites DNAPL study. Field instruments are checked and calibrated prior to beginning the field program and daily before use to verify that instruments are in good working order. Routine preventive maintenance procedures for PID are specified in the relevant operation manual and discussed in Section 6 of this QAPP. Additional details on the field equipment to be used in this project are provided in applicable procedures specified in the Field Sampling Plan.

11.2 Laboratory Instrument Routine Maintenance Activities

As part of the laboratory QA/QC program, a routine preventive maintenance program will be conducted by the laboratories to minimize the occurrence of instrument failure or other system malfunction. The laboratory workload will be scheduled to accommodate planned downtime required to complete routine maintenance procedures. Trained operators will complete routine maintenance procedures (e.g., changing oven fans, replacing electronic control boards, changing vacuum pump oil, cleaning, etc.) for GC/MS instruments. An inventory of spare parts will be maintained to facilitate timely repair of instruments and minimize downtime. This maintenance program, including a schedule of required maintenance tasks, is summarized on Table 11.1.

When routine maintenance procedures do not correct a problem with instrumentation, outside repair services will be available on a next day basis. The laboratory will not maintain test equipment to be used in the maintenance of instrumentation; rather, service representatives will bring the necessary test equipment for the service call.

Records of preventive maintenance activities for each piece of equipment will be maintained in Calibration and Maintenance log books assigned to that instrument. Preventive maintenance performed during the project will be noted in the field logbook and the instrument Calibration and Maintenance log book.

11.3 Inspection/Acceptance Requirements for Supplies and Consumables

Supplies and spare parts will be maintained for both field and laboratory instruments to assure timely completion of sample screening and analysis. For field work, critical spare parts such as batteries will be kept on-site to reduce downtime. Backup instruments and equipment will be available on-site or within 1 day shipment to avoid delays in the field schedule. An inventory of spare parts will also be kept on hand in order to complete the routine maintenance tasks described in Section 11.2.

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

TABLES

TABLE 11.1
LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

(See following pages)

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
VM Service Schedule								
Column							X	Replace as needed.
Rough Pump							X	Change oil as needed
Diffusion Pump							X	Change oil as needed.
Source							X	Clean as needed.
Injection Port			X					Inspect septa, sleeve, and seal monthly. Replace as needed.
Autotune		X						Run autotune weekly. Place printout in notebook.
Air/Water Check		X						Run check program weekly. Place printout in notebook.
VM Purge and Trap Service Schedule								
Sorbent Trap							X	Change as needed.
Purge Flow		X						Inspect weekly & record. Adjust as needed.
VG Service Schedule								
Column							X	Replace as needed.
Septum							X	Replace as needed.
Gas Cylinder	X							Inspect daily. Change when pressure reads <500psi.
Hydrocarbon Moisture Trap							X	Replace as needed.
VG Purge and Trap Service Schedule								
Sorbent Trap							X	Change as needed.
Purge Flow		X						Inspect weekly. Adjust as needed.
SM Service Schedule								
Column/Injector/Splitless Disc							X	Change sleeve and disc as needed. Clip column or replace as needed.
Septum	X							Replace daily.
Autosampler							X	Clean or replace syringe as needed.
Source							X	Clean & perform maintenance as needed.
Rough Pump							X	Change oil as needed.
Autotune		X						Run autotune weekly. Place printout in notebook.
Split Vent Traps/Filters							X	Replace as needed.

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	S A	A	AN	
SG Service Schedule								
Septa							X	Replace as needed.
Injector Liner							X	Replace as needed.
Guard Column							X	Cut front of guard column as needed.
Column							X	Replace as needed.
Zymark Extract Concentrator Service Schedule								
Bath		X						Change water, scrub bath, and dust outside weekly.
Temperature Verification		X						Verify bath temperature and adjust weekly.
Sensor Diagnostic Test		X						Check each position and adjust weekly.
TCLP Rotators Service Schedule								
Semivolatiles/Metals Rotator		X						Check rotation weekly.
IC Service Schedule								
Conductivity	X							Record daily.
Pressure	X							Record daily.
Guard Column	X							Check daily.
Eluent	X							Check daily.
Pumps	X							Prime daily.
Analytical Column	X							Check daily.
Suppressor	X							Check for leaks and record flow daily.
Autosampler	X							Check daily.
Pressure Points	X							Record daily.
HPLC Service Schedule								
Pressure	X							Document equilibrium pressure daily.
Flow		X						Check weekly.
Guard Column	X							Check daily.
Solvent	X							Check level daily.
Pumps	X							Check daily.
UV Detector	X							Record energies daily.
FL Detector	X							Check daily.
Autosampler	X							Check daily.

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
FID Service Schedule								
Septa/Sleeve		X						Replace weekly.
Signal	X							Record daily.
Autosampler							X	Clean or replace syringe, arm, needles, and tubing as needed.
Gas Cylinder	X							Inspect daily. Replace when pressure <500psi.
Column							X	Replace as needed.
Autoclave Service Schedule								
Pressure Verfication	X							Check and document daily. Replace gauge or seals as needed.
Autoclave	X							Inspect and refill daily. Drain as needed.
Temperature Verification	X							Check thermometer daily. Replace as needed.
Cleaning		X						Wash with soapy water weekly. Visually inspect for leaks and degradation.
Timer				X				Check with stopwatch quarterly. Replace as needed.
Seals	X							Visually inspect daily and replace as needed.
Autoanalyzer (TRAACS/LACHAT) Service Schedule								
Pump Platen							X	Replace as needed.
Pump Tubes							X	Replace as needed.
Flow Cell							X	Inspect and clean as needed.
Conductivity Meter Service Schedule								
Cell							X	Replatinize when 1 umho/cm range exceeds 90-100% and when erratic readings cannot be corrected. Replace as needed.
TOC Analyzer Service Schedule								
Catalyst							X	Replace as needed.
Meters			X					Check against internal flow meter monthly.
Detector Windows		X						Check and clean weekly.
Humidifiers							X	Fill levels as needed.
Syringe							X	Perform zero-point detection of syringe pump as needed.

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Konelab Service Schedule								
Water Lines			X					Clean with Hypochlorite solution monthly.
Sample Probe	X							Clean and inspect daily.
DI Water Carboy							X	Rinse and refill as needed.
ICAP Service Schedule								
Pump Tubing	X							Change daily.
Nebulizer							X	Clean as needed.
Filters			X					Inspect monthly. Clean or replace as needed.
Torchinner Tip		X						Inspect weekly. Clean or replace as needed.
Zeeman Furnace AA Spectrophotometer Service Schedule								
Sampler Syringe	X							Check for air daily. Flush syringe as needed.
Graphite Tubes	X							Inspect daily. Replace as needed.
Graphite Electrodes				X				Inspect quarterly. Replace if worn.
Quartz Windows	X							Remove and clean daily.
Graphics	X							Analyze high standard and blank daily. Adjust program as needed.
Leeman PS200 Mercury Analyzer and Autosampler Service Schedule								
Pump Tubing	X							Inspect daily. Replace as needed.
Standard Cup	X							Inspect daily. Replace as needed.
Drying Tube	X							Inspect daily. Replace as needed.
Mixing Coil		X						Inspect weekly. Clean or replace as needed.
Mercury Lamp							X	Clean and replace as needed.
Aperture	X							Check reading daily.

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12.0 PROCEDURES TO ASSESS DATA QUALITY OBJECTIVES

12.1 Accuracy Assessment

In order to evaluate the accuracy of laboratory results, LCSs and MS/MSDs will be prepared at the frequency shown on Table 3.4 by spiking with VOCs and SVOCs prior to analysis. For the LCS, the ratio between the measured concentration and the known concentration in the spiked sample converted to a percentage is equal to the percent recovery. For MS/MSDs, the difference between the measured concentration in the spike and the concentration in the native sample is divided by the known spike concentration to obtain the percent recovery, as follows:

$$\%R = \frac{\textit{Measured Concentration in Spike Sample} - \textit{Concentration in Native Sample}}{\textit{Known Spike Concentration}} \times 100$$

Daily tabulations for each commonly analyzed organic compound will be maintained on instrument-specific, matrix-specific, and analyte-specific bases. Control charts of results obtained from LCS will be maintained for selected organic analytes to track the accuracy of laboratory data

12.2 Precision Assessment

Spiked samples will be prepared by selecting a sample at random from each sample shipment received at the laboratory, dividing the sample into equal aliquots, and then spiking each of the aliquots with a known amount of analyte. The duplicate samples will then be included in the analytical sample set. The splitting of the sample allows the analyst to determine the precision of the preparation and analytical techniques associated with the duplicate sample. The RPD between the spike and duplicate spike (or between MS and MSD) will be calculated as follows:

$$RPD = \frac{\textit{Concentration in Spike } 1 - \textit{Concentration in Spike } 2}{0.5(\textit{Concentration in Spike } 1 + \textit{Concentration in Spike } 2)} \times 100$$

12.3 Completeness Assessment

Completeness is the ratio of the number of valid sample results to the total number of samples analyzed with a specific matrix and/or analysis. After analytical testing, the percent completeness will be calculated as follows

$$\textit{Completeness} = \frac{(\textit{number of valid measurements})}{(\textit{number of measurements planned})} \times 100$$

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13.0 CORRECTIVE ACTION

Corrective action will be taken to identify, recommend, approve, and implement measures to remedy unacceptable procedures or out-of-control performances potentially affecting data quality. Corrective actions may be required for i) non-conformance with procedures specified by the QAPP, ii) malfunction of sampling or analytical equipment, or iii) changes in sampling network or frequency. Non-conformances include those instances of conducting activities outside the requirements of the QAPP (i.e., missing holding times or detecting blank contamination). Analytical and equipment problems may occur during sampling, sample handling, sample preparation, or laboratory analysis. Modifications in the sampling network may result from inaccessible locations or from inadvertent omissions in sample collection.

Any non-conformance to quality control procedures specified in the QAPP will be identified, reported, and corrected. If the non-conformance is identified during sample collection or analysis, corrective action will be implemented immediately by the field technician or laboratory analyst. If the non-conformance is identified during an internal/external audit or third-party data validation, corrective action will be implemented after notification of the Solutia Project Manager, the GSI Project Manager, and/or the Laboratory Project Manager. The Solutia Project Manager will communicate the need for corrective action and the planned remedy to the U.S. EPA Project Coordinator. Any corrective actions taken during the course of the DNAPL Study will be documented in the final project report described in Section 14 of this QAPP.

13.1 Field Corrective Action

13.1.1 Corrective Action for Procedural Non-Conformances

The GSI Field Operations Manager and Field Technical Staff will be responsible for reporting suspected technical or QA non-conformances or deficiencies to the GSI Project Manager. The GSI Project Manager will be responsible for ensuring that any necessary corrective actions are implemented. Non-conformances potentially affecting data quality will be brought to the attention of the Solutia and U.S. EPA Project Managers as soon as practical. If appropriate, the GSI Project Manager will suspend additional work depending on the nature of the non-conforming activity until the corrective action is completed. The GSI Project Manager will ensure that corrective action for the non-conformance is completed by evaluating and controlling additional work on non-conforming items, determining appropriate action, and communicating with concerned persons via telephone, e-mail, or other medium.

13.1.2 Corrective Action for Changes in Sampling Network

The Contractor Field Operations Manager will communicate work plan modifications to project management for review and approval prior to implementation of significant modifications to the QAPP. In order to avoid unnecessary project delays, minor field adjustments (e.g., moving a sampling location less than 25 ft to avoid an obstruction) will be made at the discretion of the GSI Field Operations Manager and implemented without prior approval from project management, provided other health and safety considerations have been addressed (e.g., utility clearance). Such modifications will be recorded in the field logbook and brought to the prompt attention of project management. The GSI or Solutia Project Manager will then review the modification to ensure that the modification does not compromise project quality assurance objectives. GSI Field Technical Staff will not initiate work program modifications without prior communication with the GSI Field Operations Manager.

Significant plan modifications will be implemented only after obtaining the approval of the GSI Project Manager and the Solutia Project Manager. Program changes will be documented and copies of the affected document will be distributed to recipients via e-mail or other medium. The GSI Project Manager will be responsible for the controlling, tracking, and implementation of the identified changes. A discussion of field program modifications will be included in the final project report.

If the proposed modification has the potential to adversely impact attainment of project QA objectives, the U.S. EPA Project Manager will be notified while the sampling crew is still in the field. Such a situation would result if i) a sampling location were to be eliminated; ii) a sampling location were to be moved a significant distance from its designated location owing to access limitations or obstructions; or iii) sampling frequency were to be decreased. Possible corrective actions could include i) re-mobilization to collect additional samples, or ii) evaluation to determine if data already collected were sufficient to satisfy QA objectives.

If the Solutia and GSI Project Managers determine that the modification will not adversely impact the achievement of project QA objectives, no further action will be taken and a summary of the findings will be included in the final project report. If the modification has the potential to adversely impact the achievement of project QA objectives, additional locations will be sampled or additional samples will be collected and the findings documented in the final project report.

13.1.3 Field Corrective Action Reports

In all cases in which corrective actions of field procedures are required, a description of the nature of the problem, an evaluation of the cause, if known, and the action taken will be prepared by the GSI Field Operations Manager or QA Manager and distributed by e-mail, U.S. mail, or other appropriate medium. The following topics will be discussed:

- Where did the out-of-control event occur (site, location, etc.)?
- When did the incident occur and when was it corrected?
- What was the nature of the out-of-control event?
- Who discovered the out-of-control incident, verified the incident, and corrected the problem?
- What was the method number and name of the test?
- What was the disposition of the test or control and/or instrument?
- What was the nature of the corrective action?
- What will be done to prevent the reoccurrence of the problem?
- Why did the incident happen (if scientific explanation is available)?

A copy of the subject control data and other information describing the non-compliant condition will be included in the final project report. Deficiencies identified during the data validation and assessment process will also be included in the final project report.

13.2 Laboratory Corrective Action

Data packages prepared by the laboratory will include a discussion of the QC problems encountered and corrective actions taken. If an out-of-control event or potential out-of-control event is noted in the laboratory, an investigation and corrective action will be taken appropriate to the analysis and the event. Laboratory corrective action may be required if any of the following occur:

- QC data are outside the warning or acceptable windows for precision and accuracy,
- Blanks contain target analytes above acceptable levels,
- Undesirable trends are detected in spike recoveries or RPDs between duplicates,
- Unusual changes in detection limits are noted,
- Deficiencies are detected by the QA Department during internal or external audits or from the results of performance evaluation samples, or
- Inquiries concerning data quality are received.

The Laboratory QA Manager will be responsible for implementing laboratory corrective action. Individual analysts will be responsible for assessing the results from sample analysis. Results not meeting applicable criteria will be reported to a supervisor who will recommend a corrective action to be implemented by the section manager, the QC chemist and the QA/QC Supervisor. The Laboratory QA Manager will be responsible for ensuring that corrective actions are taken, as appropriate, in the following situations:

- ***Out-of-Control Criteria:*** An out-of-control situation will exist when a blank, calibration standard, laboratory control sample, sample replicate, or spike recovery analysis fails to meet applicable quality control criteria. Corrective action procedures are often handled at the bench level by the analyst who reviews the preparation for possible errors, checks the instrument calibration, spike and calibration mixes, and instrument sensitivity. If the out-of-control situation cannot be remedied by the analyst, an investigation to determine the cause of the problem will be undertaken by the analyst and department supervisor, and a Quality Assurance Action Report will be initiated. Analyses completed during the out-of-control situation will be repeated after the out-of-control situation has been corrected. If the problem persists or cannot be identified, the matter will be referred to the laboratory supervisor, manager and/or QA Department for further investigation. After resolution, the corrective action procedure will be documented and filed with the QA Department.
- ***Warning Criteria:*** Corrective measures will be implemented when one of the following two conditions occurs: i) quality assurance data for blanks, laboratory control samples, sample replicates, or matrix spikes exceed two standard deviations of applicable limits or ii) a trend or shift is observed for the reference standard. Provided other criteria are within applicable limits, samples need not be re-analyzed. A Quality Assurance Corrective Action Report will be initiated by the

analyst and the Laboratory Supervisor, and corrective action will be implemented prior to analyzing additional samples. If the situation occurs with the next sample batch, an out-of-control situation exists, and steps outlined above are taken. If matrix interference is indicated by out-of-control replicate analyses or matrix spike recovery data, re-analysis of a sample batch is necessary only when other QC data do not meet applicable specifications.

- ***Performance Audit:*** If the laboratory fails to meet applicable requirements reviewed during a performance of systems audit, corrective action will be taken. The QA/QC coordinator will notify the Laboratory Project Manager and the USEPA QA Manager in the event of a corrective action taken in response to an audit. Applicable federal and state guidelines and requirements regarding response to audit findings are observed by laboratory.

13.3 Corrective Action During Data Validation and Data Assessment

The GSI QA Manager will review analytical reports generated by STL Savannah and PTS prior to data use and filing. Upon receiving data validation or data assessment results, the GSI QA Manager will identify the need for corrective action and notify concerned persons by telephone, e-mail, or other appropriate medium. Specified corrective action will be developed to assure meeting required QA objectives. The GSI Project Manager and the Laboratory Project Managers will be responsible for implementing corrective actions in the field and laboratory, respectively. Corrective action required may include re-sampling, collecting additional samples, or re-measurement of field parameters. The laboratory may be required to repair or re-calibrate instrumentation, re-inject or re-analyze samples, or provide additional raw data. Proposed and implemented corrective actions will be documented in the final project.

14.0 QUALITY ASSURANCE REPORTS TO MANAGEMENT

The final report for the Sauget Area 1 Sites DNAPL Study will be the responsibility of the Solutia Project Manager, as supported by the GSI Project Manager. The final report will contain a section identified as the Project QA Report that addresses data quality, including the accuracy, precision, and completeness of the data, results of any performance or system audits, and any corrective action needed or taken during the project.

14.1 Contents of Project QA Report

The QA report will contain i) results of field and laboratory audits conducted during the time period covered by the report, ii) an assessment of QA results with respect to data quality objectives, iii) a summary of corrective actions that may have been implemented, and iv) results of any corrective action activities. If applicable, references to QAPP modifications will be highlighted.

14.2 Frequency of QA Reports

The Project QA Report will be prepared on a one-time basis and submitted in conjunction with the final report for the DNAPL Study.

14.3 Individuals Receiving/Reviewing QA Reports

Individuals receiving a copy of the QA report will be the following: i) U.S. EPA Project Manager, ii) U.S. EPA QA Manager, iii) Solutia Project Manager, iii) GSI Project Manager, iv) GSI QA Manager, vi) STL Savanna Project Manager, and vii) PTS Project Manager.

15.0 REFERENCES

USEPA, 1994a. *Guidance for the Data Quality Objectives Process*, U. S. Environmental Protection Agency.

USEPA, 1994b. *National Functional Guidelines for Organic Data Review*, U.S. Environmental Protection Agency, December 1994.

USEPA, 1998. *Region 5 RCRA QAPP Instructions,* U. S. Environmental Protection Agency. Revision: April1998.

APPENDICES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

APPENDICES

APPENDIX A:
LABORATORY STANDARD OPERATING PROCEDURES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

APPENDIX A
LABORATORY STANDARD OPERATING PROCEDURES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

EPA, API or ASTM Ref. Method	SOP No.	Title/Description
Not Applicable	AN53:03.11.02:0	Maintenance Procedures for Laboratory Instrumentation
5310B	BA08:03.22.02:0	Total Organic Carbon in Soils and Sediments
Not Applicable	CA80:04.28.00:7	Data Generation, Entry, Review, Approval, and Reporting
Not Applicable	CA90:08.27.02:2	Procedure for the Determination of Method Detection Limit (MDL)
Not Applicable	CA92:08.21.98:0	Evaluation of IDOCs
Not Applicable	CU01-S:04.05.02:3	Routine Sample Custody Procedures: Receipt, Log Number Assignment, and Distribution of Field Samples
Not Applicable	CU02-S:07.10.98:0	Internal Chain-of-Custody
Not Applicable	CU35:04.30.99:2	Procedure for Contaminant-Free Sample Containers
3510/3520/3550/ 3640/8270C	SM05:08.27.02:7	Semi-Volatile Compounds by GC/MS
8010/8015/ 8020/8021	VG05:01.09.02:5	Volatile Compounds in Water, Soil, and Waste by Gas Chromatography
8260B	VM20:11.12.99:4	Volatile Compounds by GC/MS (EPA 8260B)
5021, 5030, 5035	VM21:08.27.02:0	Preparation, Screening, and Storage of Volatiles Samples
245.1, 7470, 7471	ME28:1.30.04:3	Mercury Preparation and Analysis
3050B	ME51:01.30.04:3	Digestion procedures for ICP: Total Metals in Soils, Sediments, Wastes, Tissues, and Oils.
200.7, 6010	ME70:03.07.01:7	Elements by ICP
3580	EX42:07.06.98:0	Waste Dilution Extraction
8081A, 8082,608	SG45:01.30.02:7	Organochlorine Pesticides and PCBs by GC
8151A, 615, 515.1	SG65:11.05.02:5	Chlorinated Herbicides

APPENDIX A
LABORATORY STANDARD OPERATING PROCEDURES

QAPP for Work Plan for DNAPL Characterization and Remediation Study

Sauget Area 1 Sites
Sauget, Illinois

3510	EX45-S:04.24.02:3	Extraction of Chlorinated Herbicides in Waters, Soils and Wastes
8280	SM10:02.06.02:5	Dioxins and Furans
ASTM D425M-88	NA	Free Product (NAPL) Mobility – Centrifugal Method
ASTM D421/422M	NA	Sample Preparation for Particle Size Analysis Procedure
Dean Stark, API RP 40	NA	Pore Fluid Saturations – Distillation Extraction Procedure
Dean Stark, API RP 40	NA	Pore Fluid Saturations – Drying Procedure
Dean Stark, API RP 40	NA	Pore Fluid Saturations – Distillation Extraction Flow Chart
ASTM D445	NA	Viscosity of NAPL Procedure
ASTM D445	NA	Viscosity of Water Procedure
ASTM D971	NA	Determination of Apparent Surface and Interfacial Tension
Walkley-Black	NA	Total Organic Carbon Procedure
ASTM D422-63	NA	Particle Size by Dry Sieve Procedure
ASTM D2937-94	NA	Dry or Native Bulk Density Procedure
API RP 40	NA	Determination of Total Porosity Procedure

MAINTENANCE PROCEDURES FOR LABORATORY INSTRUMENTATION

Approved by:

R. Wayne Robbins   2 April 2002
R Wayne Robbins   Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the general maintenance procedures for laboratory instrumentation.

2.0 SUMMARY OF METHOD AND DEFINTIONS

2.1 A maintenance log is kept for each piece of laboratory instrumentation, detailing all maintenance performed on the instrument. Routine repairs and maintenance are performed and documented by the analyst responsible for the particular instrument. Non-routine maintenance is signed and dated by the analyst or repair technician.

Maintenance contracts are carried for most instrumentation and close contact is maintained with service personnel to provide optimal instrument functioning.

An extensive spare parts inventory is maintained for routine repairs, consisting of GC detectors, AA lamps, fuses, printer heads, flow cells, tubing, certain circuit boards, and other common instrumentation components. Since instrumentation is standardized throughout the laboratory network, spare parts and components can be readily exchanged among the network.

2.2 Contingency Plan

In general, the laboratory has at least one backup unit for each critical unit. In the event of instrument failure, portions of the sample load may be diverted to duplicate instrumentation, the analytical technique switched to an alternate approved technique (such as manual colorimetric determination as opposed to automated colorimetric determination), or samples shipped to another properly certified or approved STL location. STL Savannah is part of a voluntary network of laboratories within the STL umbrella with STL Tallahassee, STL Mobile, and STL Tampa.

3.0 SAFETY

See the instrument manufacturer's manual or analytical SOP for safety concerns for each instrument. Any instrument that is deemed to be malfunctioning must be clearly marked and taken out of service. When instrument maintenance requires that the instrument be shut down, the guidelines in SOP CA15: Energy Isolation LockOut/TagOut Procedures should be followed.

4.0 PROCEDURES

4.1 Routine preventive maintenance procedures for laboratory instrumentation are given in Table 1. The service intervals listed in Table 1 are as follows: D=daily; W=weekly; M=monthly; Q=quarterly; SA=semi-annually; A=annually; AN=as needed.

4.2 Maintenance Log

A maintenance log must be established for each instrument in the laboratory. The following information must be recorded in the log:

-instrument designation and serial number
-the date that the instrument was installed
-all maintenance that is performed on the instrument including:
  - analyst or technician performing the maintenance
  - date the maintenance was performed
  - detailed explanation of the reason for the maintenance
  - resolution of the problem and the date of return to control
-all service calls from instrument representatives
-inclusive dates that instrument was out of service

Routine preventive maintenance may be recorded on document-controlled forms instead of in the maintenance log.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of analytical personnel to perform the instrument maintenance in accordance with the minimum guidance given in this SOP and to bring any problems or potential problems with the instrumentation to the supervisor, technical manager, or laboratory manager. It is the responsibility of all analytical personnel to safely operate and maintain the instruments in accordance with the manufacturer's guidelines and STL policy.

5.2 It is the responsibility of department supervisors, in conjunction with the QA Manager, to ensure that maintenance is properly documented and that the records are complete.

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
VM Service Schedule								
Column							X	Replace as needed.
Rough Pump							X	Change oil as needed
Diffusion Pump							X	Change oil as needed.
Source							X	Clean as needed.
Injection Port			X					Inspect septa, sleeve, and seal monthly. Replace as needed.
Autotune		X						Run autotune weekly. Place printout in notebook.
Air/Water Check		X						Run check program weekly. Place printout in notebook.
VM Purge and Trap Service Schedule								
Sorbent Trap							X	Change as needed.
Purge Flow		X						Inspect weekly & record. Adjust as needed.
VG Service Schedule								
Column							X	Replace as needed.
Septum							X	Replace as needed.
Gas Cylinder	X							Inspect daily. Change when pressure reads <500psi.
Hydrocarbon Moisture Trap							X	Replace as needed.
VG Purge and Trap Service Schedule								
Sorbent Trap							X	Change as needed.
Purge Flow		X						Inspect weekly. Adjust as needed.
SM Service Schedule								
Column/Injector/Splitless Disc							X	Change sleeve and disc as needed. Clip column or replace as needed.
Septum	X							Replace daily.
Autosampler							X	Clean or replace syringe as needed.
Source							X	Clean & perform maintenance as needed.
Rough Pump							X	Change oil as needed.
Autotune		X						Run autotune weekly. Place printout in notebook.
Split Vent Traps/Filters							X	Replace as needed.

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
SG Service Schedule								
Septa							X	Replace as needed.
Injector Liner							X	Replace as needed.
Guard Column							X	Cut front of guard column as needed.
Column							X	Replace as needed.
Zymark Extract Concentrator Service Schedule								
Bath		X						Change water, scrub bath, and dust outside weekly.
Temperature Verification		X						Verify bath temperature and adjust weekly.
Sensor Diagnostic Test		X						Check each position and adjust weekly.
TCLP Rotators Service Schedule								
Semivolatiles/Metals Rotator		X						Check rotation weekly.
IC Service Schedule								
Conductivity	X							Record daily.
Pressure	X							Record daily.
Guard Column	X							Check daily.
Eluent	X							Check daily.
Pumps	X							Prime daily.
Analytical Column	X							Check daily.
Suppressor	X							Check for leaks and record flow daily.
Autosampler	X							Check daily.
Pressure Points	X							Record daily.
HPLC Service Schedule								
Pressure	X							Document equilibrium pressure daily.
Flow		X						Check weekly.
Guard Column	X							Check daily.
Solvent	X							Check level daily.
Pumps	X							Check daily.
UV Detector	X							Record energies daily.
FL Detector	X							Check daily.
Autosampler	X							Check daily.

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	S A	A	AN	
FID Service Schedule								
Septa/Sleeve		X						Replace weekly.
Signal	X							Record daily.
Autosampler							X	Clean or replace syringe, arm, needles, and tubing as needed.
Gas Cylinder	X							Inspect daily. Replace when pressure <500psi.
Column							X	Replace as needed.
Autoclave Service Schedule								
Pressure Verfication	X							Check and document daily. Replace gauge or seals as needed.
Autoclave	X							Inspect and refill daily. Drain as needed.
Temperature Verification	X							Check thermometer daily. Replace as needed.
Cleaning		X						Wash with soapy water weekly. Visually inspect for leaks and degradation.
Timer				X				Check with stopwatch quarterly. Replace as needed.
Seals	X							Visually inspect daily and replace as needed.
Autoanalyzer (TRAACS/LACHAT) Service Schedule								
Pump Platen							X	Replace as needed.
Pump Tubes							X	Replace as needed.
Flow Cell							X	Inspect and clean as needed.
Conductivity Meter Service Schedule								
Cell							X	Replatinize when 1 umho/cm range exceeds 90-100% and when erratic readings cannot be corrected. Replace as needed.
TOC Analyzer Service Schedule								
Catalyst							X	Replace as needed.
Meters			X					Check against internal flow meter monthly.
Detector Windows		X						Check and clean weekly.
Humidifiers							X	Fill levels as needed.
Syringe							X	Perform zero-point detection of syringe pump as needed.

TABLE 1 LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE

EQUIPMENT ITEM	Service Interval							SERVICE LEVEL
	D	W	M	Q	SA	A	AN	
Konelab Service Schedule								
Water Lines			X					Clean with Hypochlorite solution monthly.
Sample Probe	X							Clean and inspect daily.
DI Water Carboy							X	Rinse and refill as needed.
ICAP Service Schedule								
Pump Tubing	X							Change daily.
Nebulizer							X	Clean as needed.
Filters			X					Inspect monthly. Clean or replace as needed.
Torchinner Tip		X						Inspect weekly. Clean or replace as needed.
Zeeman Furnace AA Spectrophotometer Service Schedule								
Sampler Syringe	X							Check for air daily. Flush syringe as needed.
Graphite Tubes	X							Inspect daily. Replace as needed.
Graphite Electrodes				X				Inspect quarterly. Replace if worn.
Quartz Windows	X							Remove and clean daily.
Graphics	X							Analyze high standard and blank daily. Adjust program as needed.
Leeman PS200 Mercury Analyzer and Autosampler Service Schedule								
Pump Tubing	X							Inspect daily. Replace as needed.
Standard Cup	X							Inspect daily. Replace as needed.
Drying Tube	X							Inspect daily. Replace as needed.
Mixing Coil		X						Inspect weekly. Clean or replace as needed.
Mercury Lamp							X	Clean and replace as needed.
Aperture	X							Check reading daily.

SEVERN TRENT SERVICES

TOTAL ORGANIC CARBON IN SOILS AND SEDIMENTS

Approved by:

R. Wayne Robbins   27 March 2002
Date

Title: Technical Manager, QA

STL X Savannah ___ Tallahassee ___ Mobile ___ Tampa

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of total organic carbon (TOC) in soils, sediments, and other solids. The preparation steps for soils, necessary to remove inorganic carbon from the sample, also removes volatile organic compounds (VOC); therefore, TOC is essentially non-volatile organic carbon.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria are given in the current revision of the *Laboratory Quality Manual* prepared by and for STL Savannah. The nominal RL for soils is 1000mg/kg, dw.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1.1 A small aliquot of homogenized sample is dried overnight at 105C. The sample is crushed to form a powder. Approximately 100mg (0.100g) of dried sample is transferred to a quartz boat, and the sample is treated with 6N HCl to convert the inorganic carbon to carbon dioxide. The sample is dried again at 105C. The sample is then transferred to the instrument where the carbon is converted to carbon dioxide at 900C. The carbon dioxide is measured by an infrared spectrophotometer. Standards, prepared from sucrose, are prepared and analyzed in the same manner as the samples.

2.2 This procedure is based on the guidance in EPA Region II document entitled "Determination of Total Organic Carbon in Sediment", circa 1986 (the "Lloyd Kahn Method").

3.0 SAFETY

3.1 The analyst must protect herself/himself from exposure to the sample matrix. Many of the samples analyzed for carbon content are potentially hazardous. The analyst must wear protective clothing (lab coat or apron), eye protection (eyeglasses or face shield), and disposable gloves when handling the samples.

3.2 The furnace on the carbon analyzer and on the soil analyzer must be cooled to room temperature before maintenance can be performed. The temperature of the analyzer furnace can reach 900C. The analyst must be very careful to avoid touching these very hot surfaces.

3.3 Care must be taken when handling hydrochloric acid (HCl) and solutions of hydrochloric acid. The 2N HCl must be handled with caution. This acid will cause chemical burns and destroy unprotected clothing. The analyst must also use extreme caution when adding acid to soil samples. The acid should be added slowly to minimize potentially violent reactions that will splatter acid.

3.4 The carrier gas MUST remain on while the instrument is in operation. The analyst must ensure that there is sufficient carrier gas available in the tank to complete the run. Failure to have carrier gas running through the instrument while the combustion furnace is at the operating temperature may result in melting of the combustion tubes.

3.5 The Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure are available for inspection and review by each analyst at each lab division. The MSDS contain information on the potential hazard that each reagent poses and the guidelines for safely handling the reagent.

4.0 INTERFERENCES

It is very important that the inorganic carbon be removed from the sample prior to the direct determination of the TOC (non-purgeable TOC). Failure to remove the inorganic component of the sample may result in artificially high TOC results.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Soil and sediment samples are routinely collected in 125-ml amber glass containers with minimum headspace. The samples are iced at the time of collection and are maintained at 4C +/- 2C until the time of analysis. The maximum hold time for soil and sediment samples is 28 days from the date of collection.

6.0 APPARATUS AND MATERIALS

6.1 OI Analytical Soil Module

6.2 Volumetric pipets and microsyringes

6.3 Volumetric flasks

6.4 Disposable transfer pipets

6.5 Quartz boats, closed cup

6.6 Aluminum pans

6.7 Ultra pure compressed air, regulator, and appropriate fittings. The compressed air must contain less than 1ppm of carbon dioxide. This gas is used as the carrier and sparge gas for the analysis of aqueous samples.

6.8 Oxygen, regulator, and appropriate fittings. The oxygen is used as the carrier gas in the analysis of soil samples.

7.0 REAGENTS

All reagents must be tracked according to SOP AN44: *Reagent Traceability*.

7.1 Reagent water, lab-generated deionized water

7.2 Hydrochloric acid (HCl) - concentrated, reagent grade, or better.

7.3 Hydrochloric acid solution (50% HCl) - Add approximately 400mL of reagent water to a 2.0-L beaker. Place the beaker on a magnetic stir plate located under a hood. Add a Teflon stir bar to the reagent water and turn the stir plate on. SLOWLY and CAREFULLY add 500mL of concentrated HCl to the beaker in small aliquots. Hydrochloric acid is extremely toxic and has a suffocating odor. After the entire 500mL of HCl has been added, continue mixing and allow the solution to cool. After the solution has cooled, transfer it to a 1.0-L volumetric flask and dilute to volume with reagent water. This solution should be stored in a glass container. Prepare this solution every six months or as needed.

7.4 Kitty litter clay-purified at 900C.

8.0 STANDARDS

Preparation of standards must be tracked according to SOP AN41: *Standards Traceability.*

8.1 Carbon standard, sucrose, at 300mg/mL TOC

8.2 Calibration Standards

- weigh 100mg of purified kitty liter into a quartz boat for each calibration standard and calibration blank

- add the volume of stock standard in the following table to the respective quart boats

Calibration Standard	uL of 300mg/mL Stock Standard	Concentration (mg C)
Cal Blank (ICB/CCCB)	0	0
1	10	3
2	33.3	10
3 (CCV)	66.7	20
4	85	25.5

-add 100uL (0.10mL) of 6N HCl to each standard and place in oven set at 105C. After drying for a minimum of one hour, the standards are ready for analysis.

The continuing calibration verification (CCV) level is Calibration Standard 3 (20mg C). Prepare as many CCV and CCB as necessary to bracket the samples.

8.4 Initial Calibration Verification (ICV)

- weigh 100mg of purified kitty liter into a quartz boat

- add 15uL stock standard to the quart boat

- add 100uL (0.10mL) of 6N HCl and place in oven set at 105C. After drying for a minimum of four hours, the standard is ready for analysis.

8.5 Glutamic acid - reagent grade. Dry at 105 C for 2 hours. Store in dessicator until needed for analysis. Glutamic acid is used in its neat form as the LCS. The theoretical concentration of carbon in glutamic acid is 408000mg/kg or 40.8% C.

9. 0 SAMPLE PREPARATION

Soil samples for TOC analysis are dried to produce a free flowing, homogeneous sample. The dried sample is treated with concentrated HCl to convert the carbonates and bicarbonates to carbon dioxide, which evolves from the sample. Volatile carbon-containing compounds are also lost in the process.

9.1 Weigh approximately 5g to 10g of the soil or sediment sample into an aluminum pan.

9.2 Place the pan in the oven and allow the moisture to evaporate overnight at 105C.

NOTE: Heating the soil will drive off the volatile organics. The TOC measured from the soil is the non-purgeable or non-volatile component of the total organic carbon. Since the volatiles are usually very low compared to the non-volatile, the non-volatile component is reported as the TOC.

9.3 Remove the samples from the oven. Crush any lumps that may be present with a spatula or spoon and mix the sample to obtain a homogeneous sample.

9.4 Weigh 100 to 110mg of the sample into a quartz boat. Record the weight of sample to the nearest 0.1mg on the analysis log.

9.5 Prepare the method blank by adding 100mg of purified kitty liter to a quartz boat. Prepare the LCS by adding 20-25mg of glutamic acid to a quartz boat containing 100mg of purified kitty liter. Record the weight of the glutamic acid to the nearest 0.1mg.

9.5 Add approximately 0.10mL of 6N HCl to each field sample and QC item. Additional 6N HCl can be added if the soil has a high carbonate content. This step should be performed in a hood.

9.6 Place the sample boats into the oven to allow the excess HCl to evolve. After drying for a minimum of four hours, the samples are now ready for analysis.

10.0 PROCEDURE

10.1 Turn on the analyzer, set the furnace to 900C, and allow the instrument to equilibrate according to manufacturer's instructions. Follow the manufacturer's instructions for analysis of calibration, QC, and field samples.

10.2 Analyze the calibration standards, QC samples, and field samples according to the following sequence. Initial calibration must be performed initially, when calibration verification standards fail the acceptance criterion, and at a minimum, every six months. See SOP AN67: *Evaluation of Calibration Curves* for guidance in preparing and evaluating the calibration curve.

Sequence	Criteria
Initial Calibration	Minimum of three points; linear correlation coefficient >0.995
Initial Calibration Verification (ICV)	Within +/-10%
Initial Calibration Blank (ICB)	Less than RL
Method Blank	Per batch of twenty or fewer samples; less than RL
Lab Control Sample (LCS)	Per batch of twenty or fewer samples; 60-120% recovery; <30% RPD
8 Field samples	Reanalyze samples that exceed high standard at smaller sample weight
Continuing Calibration Verification (CCV)	Within +/-10% of true concentration
Continuing Calibration Blank (ICB)	Less than RL
10 Field samples	Reanalyze samples that exceed high standard at smaller sample weight
Continuing Calibration Verification (CCV)	Within +/-10% of true concentration
Continuing Calibration Blank (ICB)	Less than RL

11.0 DATA ANALYSIS/CALCULATIONS

Since the sample is dried prior to analysis, the result from the printout is given on a "dry weight basis". The weight of the soil is entered into the data system and the result is calculated as % dw. Convert the %C on a dry weight basis to mg/kg on a dry weight basis as follows:

$$TOC, mg/kg, dw = \%C(dw) \otimes 10000$$

For samples below 3mg of carbon, calculate the TOC as using the following equation:

$$TOC(mg/kg,dw) = \frac{\frac{3mgC}{Astd} \otimes Asample}{W} \otimes 1000$$

Where:
Astd = area (response) of the 3mg standard
Asample = area (response) of the sample
W = weight of sample in g (100mg =0.10g)
1000 = conversion of mg/g to mg/kg

12.0 QUALITY ASSURANCE/QUALITY CONTROL

SOP AN02 provides guidance for evaluating batch QC and calculating the accuracy and precision of the QC items. The minimum QC items for each batch includes a method blank and a lab control standard (LCS). If precision is required and requested, prepare and analyze the LCS in duplicate (LCSD).

Initial and on-going demonstration of capability must be performed in accordance with SOP CA92.

The method detection limit (MDL) must be performed annually in accordance with SOP CA90.

13.0 PREVENTIVE MAINTENACNE AND TROUBLESHOOTING

See instrument manufacturer's manuals.

14.0 WASTE MANAGEMENT AND POLLUTION CONTROL

Excess samples, standards, and reagents must be disposed in accordance with SOP CA70: *Waste Management*.

15. 0 REFERENCES

Determination of Total Organic Carbon in Sediment; USEPA Region II Environmental Services Division Monitoring Management Branch; Edison, NJ. Lloyd Kahn, QA Specialist. 7/10/86.

SEVERN TRENT SERVICES

DATA GENERATION, ENTRY, REVIEW, APPROVAL, AND REPORTING

Approved by:

R. Wayne Robb ________ 26 July 2004
Date

Title: Technical Manager, QA

STL X Savannah ___ Tallahassee ___ Mobile ___ Tampa West

1.0 SCOPE AND APPLICATION

This SOP describes the policies and guidelines used to generate, review, and report data at STL.

2.0 SUMMARY OF METHOD

Projects are logged into the Laboratory Information System (LIMS) and the sample preparation and analyses are assigned to the appropriate analytical department. After the analyses are completed, sample results with the associated QC data are reviewed by a peer analyst or the department supervisor. The data are entered into the LIMS via direct instrument interface or by manual entry via worksheets or LIMS terminal. For Level III and IV deliverables, complete data package reports (forms and/or raw data) are prepared, assembled, and reviewed by each analytical department. The final data package report is collated and archived by the Data Reporting Department. The assembled data package is then routed to the Project Manager for submittal to the client. For Level III and IV reports, the QA Department performs a secondary review for accuracy, completeness, and consistency.

3.0 PROCEDURE

3.1 Raw and Reduced Data Review

Analytical results and associated QC data are reviewed by the department supervisor or a peer analyst prior to worksheet entry. The data must be reviewed for accuracy, precision, and completeness, and signed to ensure that all method QC specifications have been met. The review includes checking the extraction, digestion, or preparation logs and all accuracy and precision data to ensure that all steps in the analysis have been completed.

3.2 Worksheets

LIMS generated worksheets are printed periodically. The analyst or designated person retrieves the department's worksheets. These worksheets list the parameters, client name, STL log number, matrix, date sampled, date due, and provide a place for results and initials.

All results are to be entered with two (2) significant figures (except for CLP or other special protocols). All additional appropriate QC listed on the worksheet **must** be noted and reported along with the sample results.

As a minimum, the LIMS worksheet(s) request QC results for method blanks and lab control standard accuracy and precision data for each analytical batch. Additional project specific QC can be initiated on the worksheets.

If any problems arise during the analysis of the sample batch, it is the responsibility of the analyst and section supervisor to bring this to the attention of the project manager, section manager, and QA manager through the nonconformance and corrective action system. (See STL SOP CA85).

3.3 Nonconformance/Corrective Action Reports

Corrective action will be initiated when data are determined to be questionable or QC criteria are out of control. For routine operational problems, the analysts correct the problem and note the problem/corrective action on the run log or bench data sheet. When formal corrective action is required, the SOP for Nonconformance and Corrective Action Procedures (CA85) is followed.

3.4 Manual Data Records

All manual records of analytical data for non-computerized analytical methods and notebook records of ancillary QC data are made with black waterproof ink. Data errors are deleted by striking through the error with a single line and writing the corrected entry beside the error, if necessary. The correction is initialed and dated by the staff member making the change. Liquid paper-type products must not be used with evidential data or any data constituting part of the quality control system.

3.5 Client Reports

3.5.1. Non-package (STL Level I & II)

After the data have been entered into the LIMS and is found to have been entered correctly, the project manager reviews the final report. The project manager must use his/her experience to properly review the data.

Some questions to ask are:

> Is the client name and address correct? Are there misspellings?

> Are the results reported to two (2) significant figures?

> Were holding times met?

> Are methods provided?

> Are the results in the proper units for the matrix? Is the % solids reported if the sample is solid/soil?

> Are the results reasonable? Does the PQL reflect the dilutions that were used? Why were dilutions necessary?

> Are all accuracy and precision values within limits? If not, is an NCR available to explain the problems encountered? Are data flags necessary? Is a case narrative necessary?

> Are footnotes and case narratives clearly stated and correct?

> Were there any nonconformance reports filed with the data? Were nonconformance samples reanalyzed? If not, why not?

> Is the COD greater than the BOD? Conductivity less than the TDS? Dissolved values less than or equal to total values?

> *Do the reported compounds "go together," i.e., when phenanthrene is present other* creosote/PAH compounds are generally present.

> Are breakdown products present? Have the results been confirmed? How close are the primary/confirmation results?

> Were modifications to the approved procedures needed to meet the requirements of the project? Were these modifications noted in a case narrative?

3.5.2 For reports that require a CLP-type data package (STL Level III, Level IV), the complete report (forms and or raw data) is prepared, assembled and reviewed by each analytical department. Each analytical department then routes copies of their section of the final report to the Data Reporting Department for final assembly. The Data Reporting staff types a case narrative and lists any modifications that were required to the approved procedures based on information listed on the Chemist Comment Sheet prepared by the analytical department. The Data Reporting Department collates, paginates, files and archives ancillary data records, and routes the final data package report to the Project Manager for submittal to the client. Prior to submission of the report to the client, the QA Department performs a secondary review on 100 % of all complete data package reports to ensure project data quality objectives are met and checks the report for accuracy, completeness, and consistency with standardized format. If any errors or discrepancies are detected, the complete data package report is returned to the respective analytical department for re-evaluation and edits, as necessary. After edits are made, the report is again reviewed to ensure that corrections were made appropriately.

For LIMS Reports and Data Package Reports, the Project Manager signs and sends the final report to the client and handles all further contact with the client.

3.6 Using CLP Flags for Non-CLP Methods

The Contract Laboratory program (CLP) requires that data be reported in a standard format. Often a client will specify that CLP data flags be used for non-CLP analyses. These requests will be specified in a pre-project plan, a site or client specific quality assurance plan, or in the laboratory worksheet notes. When CLP flags are utilized, standard STL data flags should **not** be used. See STL SOP CA83 for the current standard STL data flags/qualifiers.

3.6.1 Organic Parameters

The common CLP data flags for organic parameters (VG, SG, VM, SM, LC) include:

U - undetected; result is less than the project quantitation limit or if estimated results (J Flags) are to be reported, less than the MDL.

J - estimated; result is below the project quantitation limit but greater than or equal to the MDL.

B - target compound present in the method blank.

E - concentration of the target compound exceeds the concentration of the highest standard in the calibration curve (used only when multiple dilutions are reported as separate samples).

D - results are reported from a dilution (used only when multiple dilutions are reported as separate samples).

P - relative percent difference between primary and confirmation columns (GC or LC) or detectors (LC-
PAHs) exceed 40%.

Surrogate Recovery
If the sample is diluted so that quantitative results cannot be reported for the surrogate(s), the result is reported 0%D. This will apply only to semivolatiles and volatile samples requiring a methanol *extraction.*

EXAMPLES

Sample	Sample Result (ug/L)	Method Blank Result (ug/L)	RL (Ug/L)	MDL (ug/L)	CAL Range (ug/L)	CLP-Flagged Result	
						Sample	MB
1	<10	<10	10	2.5	10-200	10U	10U
2	5.2	<10	10	2.5	10-200	5.2J	10U
3	500 (No Dilution)	<10	10	2.5	10-200	500E	10U
3	750 (1:5 Dilution)	<10	10	2.5	10-200	750D	10U
4	8.0	3.9	10	2.5	10-200	8.0JB	3.9J
5	Col 1=0.50 Col 2=1.0 (%RPD=67%)	1.2	1.0	0.25	1.0-20	0.50JBP	1.2
6	Col 1=0.56 Col 2=0.60	<1.0	1.0	0.25	1.0-20	0.60 J	1.0U

Col 1 = primary column or detector
Col 2 = confirmation column or detector

3.6.2 Inorganic Parameters

The common CLP data flags for inorganics [ME, GE (cyanide)] include:

U - undetected; result is less than the project quantitation limit or if estimated results (J flags) are to be
reported, less than the MDL.

B - target compound present in the method blank.

E - serial dilution exceeded ±10% criteria.

M - %RSD criteria exceeded for replicate analysis; analysis repeated and results confirmed.

N - MS/MSD exceed acceptance criteria.

S - method of standard addition was used to quantify the sample.

W - (GFAA) post digestion spike recovery outside acceptance limits.

* - sample duplicate %RPD exceeded acceptance limits.

For most ME and GE work, only the U and B flags are incorporated into non-CLP work and they are used in the same manner as the corresponding organics flags.

3.6.3 Project-Specific Flags

Occasionally, situations will arise that require project-specific flags that are not defined in sections 3.6.1 and 3.6.2. In these cases, the analyst will consult with the section supervisor, QA Manager or designee, and the project manager to define the data flags. Use the letters X, Y, and Z to designate the project-specific data flag qualifiers. If more than three data qualifiers are required, a detailed case narrative must be prepared for the project. A case narrative is recommended for all projects where CLP flags are utilized.

PROCEDURE FOR THE DETERMINATION OF METHOD DETECTION LIMIT (MDL)

Approved by:

Andrea Teal   08/27/02
Date

Title: Quality Assurance Manager

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

1.0 SCOPE AND APPLICATION

The following SOP details the mechanism for the determination of the method detection limit (MDL) in accordance with 40 CFR Part 136 Appendix B.

MDL studies should be performed at the spiking levels detailed in Table 1. The spiking levels are expressed as multiples of the reporting limit (RL) in the current Laboratory Quality Manual (LQM). MDL studies must be performed annually and each time a significant change to the method occurs for all method/analyte/matrix combinations. Supporting raw data must be retained in discreet files maintained by the QA department or within the analytical department performing the MDL study.

If multiple instruments are used for the same method parameters, then the MDL should be determined on one instrument using the entire procedure (prep and analysis) and verified on all common instruments. Verification is accomplished by the analysis of a standard at or near (within a factor of two of) the calculated MDL.

It should be noted that some parameters do not lend themselves to MDL determination and as such, no MDL study should be performed for these procedures. A list of these parameters and the procedures for demonstrating sufficient test sensitivity is presented in Table 2.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 The MDL is determined statistically from data generated by the analysis of seven or more aliquots of a spiked reagent matrix and verified by the analysis of calibration standards near the calculated MDL. The MDL is determined by calculating the standard deviation of the replicate measurements and multiplying by the appropriate Students t value for a 99% confidence level and n-1 degrees of freedom.

2.2 The following steps summarize the procedure:

1) Spike a minimum of seven aliquots (typically 9-10) of clean reagent matrix (analyte-free water or sand) with the analytes of interest. (Although a minimum of seven replicates is needed, more than seven are prepared so that, in the event there is a failure of one or more of the analytes in one of the samples, the study will not have to be re-prepared.)
2) Perform all preparation and analytical procedures for the method. All initial and continuing calibration criteria must be met.
3) Evaluate and calculate the concentration of the target analytes in samples 1-7 to determine the MDL.
4) If there is an observation of an outlier due to a technical failure, such as a poor injection, contamination, poor purge, etc., then eliminate this outlier and replace with the next successive sample. Documentation of the rationale for eliminating an outlier must be provided.
5) Summarize the data using a PC spreadsheet or Chemserver module. Calculate the MDL using the equations given in this SOP. Ensure that the calculated MDL meets all associated MDL acceptance criteria as outlined in this SOP.
6) Verify the MDL analyzing a standard at or near the calculated MDL on each instrument that is used to perform a given analysis.
7) Submit MDL data and associated documentation to laboratory management for evaluation and approval.

2.2 Defintions

Method Detection Limit (MDL) – "the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyte." (40 CFR Part 136, Appendix B, July 1, 1995, Revision 1.11).

Reporting Limit (RL) – also called practical quantitation limit (PQL).

3.0- SAFETY

Safety concerns are addressed in the applicable sample preparation and analytical SOPs.

4.0 PROCEDURES

4.1 Standards

Where possible, spiking solutions should be prepared using the same materials used for calibration. All criteria related to standards traceability and viability must be met. Refer to SOP AN41: *Standard Material Traceability* for guidance. MDL spiking solutions should be prepared using a water-miscible solvent wherever possible.

4.2 Sample Preparation

All sample preparation steps performed on routine samples must be included when performing the MDL study. If a cleanup procedure is routinely used in preparation or analysis, the cleanup must also be used in the determination of the MDL.

4.2.1 Preparation of Spiking Solution
Upon determining the methods/analytes for which an MDL study is required, consult Table 1 to determine an initial spiking level.

4.2.2 Procurement of Reagent Matrix
Reagent water (water demonstrated to be free of interference for the analytes of interest, typically deionized water) is generally used for all liquid MDL studies. Some programs may require MDL studies performed in a particular discharge or "real" matrix. Consult technical staff prior to beginning such a study.

Reagent sand is used for solid MDL studies. Reagent sand may be prepared by heating or solvent rinsing "sandbox" sand prior to use. Ottawa sand is also acceptable. Alternatively, a batch of well-homogenized sand may be analyzed prior to preparation. If no analytes of interest are detected (at any level) the material may be used without further preparation. If target compounds are detected, the material must be decontaminated prior to use. Sand may be decontaminated by heating in a muffle furnace, by solvent extraction, or by acid digestion. Consult technical management to determine the correct procedure for securing an appropriate solid matrix for MDL determination.

Due to the abundance of some elements in sand, no solid material has been identified in which to perform MDL studies for several elements, specifically iron, silicon, aluminum, calcium, magnesium, and manganese. MDL determination for these elements should be conducted using procedures for solid samples, however the addition of the solid matrix should be omitted.

4.2.3 MDL Sample Prep

For the preparatory procedure used in the method for which the MDL is to be determined, prepare 7-10 replicates of reagent matrix and spike each replicate using the MDL spiking solution(s) and any other appropriate solutions required by the procedure being performed. Prepare samples using all steps indicated in the applicable SOP.

4.3 Sample Analysis

MDL samples are analyzed in the same manner as all other samples in accordance with the appropriate method SOP. All instrument performance criteria detailed in the method SOP should be met prior to analysis of MDL samples.

After sample analysis, review individual samples using normal sample review criteria (i.e., surrogate recoveries, internal standards, etc.). Tabulate results from the first seven samples analyzed in the study and review the data set as detailed below.

4.4 Evaluation of data set

After results are tabulated, evaluate each replicate for a potential outlier(s). Should any point(s) appear unusual within the data set, evaluate whether the point(s) should be reanalyzed, or rejected. If there is an observation of an outlier due to a technical failure, such as poor injection, contamination, or poor purge, etc., then this sample should be eliminated and replaced with the next successive sample.

Rejection of apparent outlier data points should be verified statistically based upon the following criteria (the Q-Test):

- Calculate the range of the results. The range is defined as the largest value minus the smallest value in the series of results.

- Calculate the difference between the suspect result and the result nearest in value to it.

- Divide the difference obtained in above step by the range to obtain the rejection quotient, Q

- Consult Table 3, below, for Q values at various degrees of freedom. If the computed value of Q is greater than the value in the Table, the result can be discarded with 95 % confidence that it was subject to some factor which did not operate on the other results. If the result is less than or equal to the Q value in the Table, the result should not be rejected and should be included in the calculation of the MDL.

- An example of this calculation is included later in this text.

4.5 MDL calculation

After determination of the data set to be used for MDL calculation is complete, calculate the average, standard deviation, and MDL for each analyte. The MDL can be calculated by selecting from Table 4, the appropriate $t_{0.99}$ value for the number of replicates used and multiplying the standard deviation of the replicates by the $t_{0.99}$ value. An example of this calculation is included later in this text.

4.6 MDL evaluation

After calculation of the MDL, the result obtained should be compared to the reporting limit and spiking level selected. Spikes performed as levels too high or too low will result in erroneous MDL values.

4.5.1 Compare the MDL to the RL. The calculated MDL must less than the RL. If the calculated MDL is not less than the RL, the study will have to be re-analyzed or, with management approval, the RL will have to be elevated.

4.5.2 Compare the calculated MDL to the spiking level. The calculated MDL must be greater than 1/10 the spiking level. If the MDL obtained is less than 1/10 the spike value, the calculated MDL may be unrealistic and should be reevaluated. An MDL verification check can be analyzed at this concentration, however, and if all verification criteria outlined below are met, then the MDL can be raised to a value 1/10 the spike concentration.

4.6 Verification of the MDL

An MDL verification standard at or near (within a factor of two) the concentration of the determined MDL must be analyzed on all instruments and columns associated with the analysis. This standard must provide qualitative identification of all analytes.

All analytes in the MDL verification check standard must be detected at a level three times the background noise. For GC/MS analyses, the MDL verification check standard must also provide a mass spectrum where qualitative identification of the compound occurs.

If the MDL verification criteria cannot be met, then the MDL study must be re-performed, or the MDL must be raised to a level that can be qualitatively identified and meets the associated criteria.

4.7 MDL Documentation and Approval

MDL data must be performed annually and submitted to laboratory management as soon as possible after completion for evaluation and approval. All associated documentation, including explicit rationale for eliminating points, Q-Test studies, and MDL verification checks must also be submitted for review.

All associated documentation must be kept on file in the QA department or within the analytical department performing the study.

5.0 RESPONSIBILITIES

5.1 It is the responsibility of laboratory management to ensure that MDL studies are scheduled, performed, and completed annually in accordance with the provisions of this SOP and STL policies.

5.2 It is the responsibility of laboratory personnel to prepare and analyze MDL samples in the same manner as routine samples in accordance with STL policies and this SOP and to forward MDL and verification studies to laboratory management for review and approval.

5.3 It is the responsibility of QA personnel to review and archive the MDL data and to provide documentation of the MDL studies when requested by laboratory management and clients.

Table 1 Suggested Spiking Levels for MDL studies	
Method	**Suggested Spiking Level**
Extractable Organics	0.5 times RL
Organics, all non-drinking water methods	0.5 times RL
Metals, ICAP/GFAA/CVAA	3-5 times Instrument IDL
Nutrients/General Parameters	1.0 times RL
Volatile Organics	1.0 times RL

TABLE 2 - Exempt Analytes and Procedures for Sensitivity Demonstration	
Analyte	Demonstrate Sensitivity By
Coliform, all	n/a
Streptococcus, all	n/a
Hydrogen ion (pH)	n/a
Redox potential	n/a
Odor	n/a
Specific Gravity	n/a
Paint Filter Liquids	n/a
Color	Lowest Platinum-cobalt standard is at reporting limit
Cyanide, amenable to chlorination	n/a
Cyanide, weak and dissociable	n/a
Cyanide, reactive	n/a
Sulfide, reactive	n/a
Temperature	n/a
Settleable matter	n/a
Flashpoint / ignitability	n/a
Residual chlorine	n/a
All radiological parameters	n/a
2,3,7,8-TCCD by 625/8270 screen	Analyze 2,3,7,8-TCDD standard @ 10 ug/ml under typical instrument conditions and ensure detection
All organic surrogate compounds	n/a
All calculated parameters (Langiler index, etc.)	n/a
Dissolved oxygen	n/a
All solids determinations performed on a solid matrix (% solids, etc.)	n/a
Salinity	n/a
THM formation potential	n/a
All titrimetric analysis	Where possible to spike analyte of interest, titrate 2 standards spiked at RL. Calculate accuracy and precision (%RPD) and ensure is within current GQAP/FQAP ranges. If outside QA ranges, technique is suspect - examine for error and repeat.
Residue, total	n/a
Residue, volatile	n/a

Table 3 Rejection Quotient, Q	
Number of Observations	$Q_{0.95}$
3	0.970
4	0.829
5	0.710
6	0.625
7	0.568
8	0.526
9	0.493
10	0.466

(from *Fundamentals of Analytical Chemistry*, 4th edition, Skoog & West, 1982.

TABLE 4 - Student's $t_{0.99}$ Values		
Number of Aliquots, (n)	**Degrees of Freedom, (n-1)**	**$t_{0.99}$**
2	1	31.821
3	2	6.965
4	3	4.451
5	4	3.747
6	5	3.365
7	6	3.143
8	7	2.998
9	8	2.896
10	9	2.821
11	10	2.746

$t_{0.99}$ is the Student's t-value for n-1 degrees of freedom

(t-values are from the "Chemical Engineer's Handbook," 4th Edition, Perry, Chilton, and Kirkpatrick, 1963.) and 40CFR Part 136 Appendix B, Revision 1.11.

APPENDIX A

Example Calculations of the MDL and Outlier Test

Seven aliquots of reagent water are spiked at 0.020mg/L and analyzed. The results for the seven aliquots are:

RESULT	concentration (mg/L)
1	0.021
2	0.018
3	0.016
4	0.022
5	0.023
6	0.019
7	0.020

The average is calculated as 0.01986
The standard deviation is calculated as 0.002410
The MDL is calculated as SD x $t_{(0.999)}$ = 0.00292 x 3.143 = 0.0077mg/L

The result 0.016 is suspected of being an outlier. The Q value is used to determine whether this result is kept or discarded.

1. The range of values is 0.024 - 0.016 = 0.008

2. The difference between 0.016 and its nearest neighbor, 0.018, is
   - 0.016 = 0.002

3. The Q value is calculated as
   Q = 0.002/0.008 = 0.25

4. Since there are seven observations: $Q_{0.95}$ value = 0.568. The calculated Q is less than the Table $Q_{0.95;}$ therefore, the result 0.016, should not be discarded and is included in the calculation of the MDL.

EVALUATION OF IDOCs

Approved by:

R. Wayne Robbins   15 Aug 2001
Date

Title: Technical Manager, QA

STL ✓ Savannah ___ Tallahassee ___ Mobile ___ Tampa West

1.0 SCOPE AND APPLICATION

The purpose of this procedure is to provide guidance for the evaluation of initial demonstration of capability (IDOC) data. In general, IDOCs are prepared and/or analyzed as a team of analysts and may not always include all members of a department. The goal of STL is to perform IDOCs when new analysts are added to the department and when a new procedure or analyte is implemented.

2.0 SUMMARY OF METHOD

After completion of the analysis of the IDOC samples, the data are summarized and evaluated against method-specified criteria. If the data falls within the criteria, the summary is archived by the QA Officer. If one or more analytes fail to meet the criteria, the data are evaluated by the department supervisor or technical manager and corrective action is taken. If no method-specific criteria are available, the criteria for similar analytes may be used or a performance evaluation sample (single or double blind) may be used to demonstrate acceptable method performance.

3.0 PROCEDURE

3.1 The IDOC is initiated by the Lab QA Officer or designated personnel. The IDOCs are logged into the LIMS and assigned a log number. The work is distributed to the various departments and the IDOC samples are prepared and analyzed in accordance with the appropriate STL SOP.

3.2 Analyses/Analytes With Defined Criteria

3.2.1 Prepare and analyze the IDOC samples in accordance with the method and STL SOP.

3.2.2 Summarize the data and calculate the mean and standard deviation.

3.2.3 Compare the mean and standard deviation to the acceptance criteria.

-If the data meet the criteria, the report is signed by the department supervisor or technical manager and the data are archived by the QA Officer.
-If one or more analytes fail to meet the criteria, the data are reviewed by the department supervisor or technical manager. Depending on the nature of the failure, several corrective actions may be taken:

1) The IDOC may be re-analyzed or re-prepped and re-analyzed and re-evaluated. If it passes, no further action is required and the report is signed and archived.

2) The IDOC may be passed
   a) if the failing compounds have demonstrated problems in the past or
   b) if the failure concerns only a few analytes and the recoveries pass but the precision fails or if the recovery is just out of the limits.

   NOTE: Some analytes may undergo chemical reactions in the presence of other analytes in the IDOC sample that would be very to be together in environmental samples.

3) Additional training of the analyst or group of analysts performing the procedure and reanalysis of the IDOCs

3.3 Analyses/Analytes Without Defined Criteria

3.3.1 *Prepare and analyze four* (4) *IDOC samples at a mid-level concentration as determined* by the calibration curve. A calibration curve should be analyzed and evaluated prior to the preparation and analysis of the IDOC samples.

3.3.2 Summarize the data and calculate the mean and standard deviation.

3.3.3 Compare the mean and standard deviation to the acceptance criteria.

Inorganic parameters: Evaluate the data against the limits in the method. If no criteria is published for an analyte, use the limits in the STL CQAP.

Organic parameters: Evaluate the data against the limits in the method. If no criteria is published for an analyte, use the accuracy and precision limits in the STL QAP. Alternatively, use recovery limits of 70-130% (SW-846 Method 8000B) for analytes with no existing in-house accuracy and precision limits.

If the analyte(s) fails the criteria, repeat the analysis. If the average is still out of the criteria, evaluate the procedure for problems in preparation and in the analysis. If no problems are detected, evaluate the data against the criteria for a similar compound-i.e., same general molecular weight and functional groups or obtain a performance evaluation sample, *if available*.

3.4 Records

Raw data area reviewed and archived in the same manner as routine samples. The final report *is retained by the QA Officer in a central location for review by auditors and* management.

SEVERN TRENT SERVICES

ROUTINE SAMPLE CUSTODY PROCEDURES-
RECEIPT, LOG NUMBER ASSIGNMENT, AND DISTRIBUTION OF FIELD SAMPLES

Approved by:

R. Wayne Robbins — Date: 24 April 2002
RWayne Robbins

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

This SOP describes the routine procedures used for receiving samples into the laboratory, checking the integrity of the samples, assignment of a sequential laboratory identification number to the samples in a given project, and the distribution of the sample to the appropriate laboratory department. This SOP is applicable to STL Savannah.

2.0 SUMMARY OF METHOD AND DEFINTIONS

2.1 Upon arrival in the laboratory, the shipping containers are opened and inspected. The temperature of the containers is measured and recorded and the contents of the shipping containers are checked against the chain-of-custody (COC) forms. If the integrity of the shipping containers or the sample containers has been compromised or if there is a discrepancy between the COC and samples, an anomaly report is initiated by the sample receipt custodian and the assigned project manager is notified. A sequential laboratory identification number is assigned in order of sample receipt from the sample receipt registry and the project number is recorded on the COC. A sample barcode label containing the project number and sample designation are affixed to each container. The samples are distributed to the appropriate laboratory department where samples are relinquished to the department and logged into the department storage areas using barcode readers. Sample preservation, if applicable, is checked by departmental analysts. The samples are then properly stored until preparation and/or analysis.

2.2 A sample is considered in custody if it is:

- in actual possession of the sampler or transferee
- in view after being in physical possession of the sampler or transferee
- sealed so that sample integrity will be maintained while in possession of the sampler or transferee
- in secured area restricted to authorized personnel

The procedures of STL Savannah are in accordance with this definition of custody. Evidence of documentation of sample collection, shipment, laboratory receipt, and custody is accomplished utilizing a chain-of-custody record (Figure 1). In addition, field samples are tracked in the laboratory using the Sample Internal Custody Log and are tracked in and out of storage areas by use of a barcode system.

3.0 SAFETY

3.1 Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 Field samples may contain hazardous waste. Caution should be exercised when opening the coolers and handling the sample containers. Unless a Material Safety Data Sheet (MSDS) is received with the samples, a strong odor from a cooler or sample container is most likely the only indicator that the sample receipt personnel will have about the nature of the sample. The receiving area supervisor and the safety officer should be immediately alerted to such samples and action taken to ensure that the samples are handled safely.

3.3 Many of the samples received by the lab contain preservatives. If contacted, these preservatives can burn unprotected skin or destroy unprotected clothing. Sample receipt personnel must wear a lab coat or apron, eye protection, and latex gloves when handling coolers or sample bottles. Sample receipt personnel must be familiar with the color codes system and the preservatives that are used in samples. The following table includes information about the preservatives:

Sample Preservative Color Code System

Special sampling containers are designated for each analysis group in the laboratory. A preservative color-code system is utilized to alert sampling teams, sample receiving personnel, and analysts handling the containers as to which preservative was added to stabilize the sample during shipment and storage. The color-coded preservative system is as follows:

PRESERVATIVE COLOR CODE KEY

ORANGE	NO PRESERVATIVE
RED	CAUTION! STRONG OXIDIZER! CONTAINS NITRIC ACID. AVOID skin and eye contact. If contact is made, FLUSH IMMEDIATELY with water.
GREEN	CAUTION! CONTAINS SULFURIC ACID. AVOID skin and eye contact. If contact is made, FLUSH IMMEDIATELY with water.
BLUE	CAUTION! STRONG CAUSTIC! CONTAINS SODIUM HYDROXIDE. AVOID skin and eye contact. If contact is made, FLUSH IMMEDIATELY with water.
TAN	Contains Zinc Acetate. AVOID skin and eye contact. If contact is made, FLUSH IMMEDIATELY with water.
YELLOW	Contains Sodium Thiosulfate. Sterilized container.
LT. BLUE	CAUTION! CONTAINS HYDROCHLORIC ACID! AVOID skin and eye contact. If contact is made, FLUSH IMMEDIATELY with water.
LT. GREY	Contains sodium bisulfate solution (VOC).
HOT PINK	Contains methanol preservative (VOC).

4.0 PROCEDURES

4.1 Sample Collection, Preservation, and Handling

Samples must be processed and distributed to the appropriate department as soon as possible. Short hold time parameters (Figure 2) and samples with RUSH status should be given priority for distribution.

4.2 Apparatus and Materials

Thermometer or measuring device calibration checked against a NIST-certified thermometer in accordance with STL SOP AN55:*Laboratory Thermometer Calibration.* Digital thermometers must be verified quarterly.

NOTE: Do not use Sharpie pens in the receiving area. These pens contain volatiles which may contaminate samples. A "Peel-off China Marker" (Faber Castell 2663) or equivalent "grease" pen may be used for labeling purposes.

4.3 Receipt, Inspection, and Acceptance of Sample Containers

The process of receiving samples into the lab and taking custody of the samples is a dynamic process. Some procedures listed in this section may be performed concurrently, although listed in different subheadings. Coolers may arrive in the lab via common courier (Federal Express, UPS, etc.), via client delivery, via courier, or via STL field crew. It may be beneficial (but not required) to record the tracking numbers of samples received via common courier.

NOTE: The lab may be requested by some clients to use a cooler checklist that documents the receipt of samples. Sample receipt personnel must be aware of these client-specific requests.

NOTE: Foreign soils must be handled in accordance with SOP AN80: *Sterilization of Foreign Soils.* Each foreign soil container must have a fluorescent green sticker affixed to the outside that reads **"FOREIGN SOIL - STERILIZE BEFORE DISPOSAL".**

4.3.1 Inspect the general condition of the coolers. Coolers with custody seals must be checked to ensure that the seal is in place. All coolers must be inspected for signs of tampering and damage. If the custody seal has been compromised or if signs of damage or tampering are evident, the assigned project manager should be notified immediately and the situation noted in an anomaly report (Figure 3).

4.3.2 Coolers that are known to contain RUSH status samples and/or samples with short hold times (Figure 2) must be checked first. Open the coolers and inspect the general condition of the contents. It is a good practice to work on the coolers on a project-by-project basis to minimize the time that samples are outside of the coolers and storage areas.

Upon receipt, check the coolers for:

- sample container temperature
- the presence of a chain-of-custody form
- the presence of broken or damaged containers
- containers with no labels or labels that are not legible

4.3.2.1 Determine the temperature of the samples by measuring the temperature of the "temperature bottle" (usually a 100ml plastic vial filled with water). Allow the thermometer to equilibrate (not to exceed one minute) and record the temperature on the Sample Internal Custody Form (Figure 5) and on the laboratory's copy of the COC. If the temperature is greater than 6C, the assigned project manager must be notified and an anomaly report must be filled out.

NOTE: The acceptance temperature for coolers is less than 6C with no frozen samples. This criterion replaces the previous criteria of 4C +/- 2C. This criterion is used as the default criteria for the generation of an anomaly report. Some states, programs, and clients may specify other acceptance criteria.

NOTE: Evidence of Cooling for Local Sampling Events (within ~50 miles of the lab):
For samples that are received into the lab immediately or soon after sampling, the cooler and sample temperature will most likely not be less than 6C. In these cases, an anomaly report is not required if the temperature is above 6C and there is ice in the container and the temperature of the container is less than ambient (room) temperature.

NOTE: If a temperature bottle is not included in the cooler, determine the temperature of the samples by inserting a thermometer between one sample container and the bubble-pack. If the samples are not wrapped in bubble-pack, wrap the sample with bubble-pack and insert the thermometer between the bubble-pack and the container. Allow the thermometer to equilibrate for two minutes. Record the temperature on the sample registry. If the temperature is not less than 6C, the assigned project manager must be notified and an anomaly report filled out. The absence of a temperature bottle and the method of determining the temperature must be recorded on the anomaly report.

NOTE: To avoid compromising the integrity of the samples, sample contents/opened containers are not to be used for temperature checks unless written instructions are delivered to the receiving area prior to sample receipt.

4.3.2.2 Compare the contents of the cooler to the COC. If there is no discrepancy between the COC and the samples, the COC is signed to indicate agreement and forwarded to project management. If there are discrepancies between the COC and samples, notify the assigned project manager and fill out an anomaly report.

- If no COC has been included in the cooler or has not been sent with the project samples, the sample receipt personnel must notify the assigned project manager and initiate a chain-of-custody using the STL Savannah form (Figure 1). This deficiency must be noted in an anomaly report.
- If sample containers are missing or have been broken or damaged beyond use, the sample receipt personnel must notify the assigned project manager and initiate an anomaly report.
- If the sample containers are not labeled or if the sample identification cannot be determined, the sample receipt personnel must notify the assigned project manager and initiate an anomaly report.

4.3.2.3 Fill out the sample registry (Figure 4). The sample registry and the COC or COC/anomaly report should agree to the number and types of containers in a given project.

4.4 Log Number Assignment

Assign a laboratory identification number (log number) to the project from the sample registry and record the log number on the COC. The log number will be affixed to each sample in the project via a barcode.

The log number is assigned using the following format:

STL division designation/year/five digit sequential log number from the sample registry

The following designations are used for the STL divisions that share the LIMS system:

S = STL Savannah	T = STL Tallahassee
M = STL Mobile	B = STL Tampa

The year is assigned using the last numeric character from the year. For example, use "0" for 2000; "1" for 2001; "2" for 2002, etc.

An example log number would be S242450: the "S" represents STL Savannah; the "2" represents the year 2001; and "42450" is the assigned sequential log number from the sample registry.

4.3.6 Prepare the appropriate number of barcode labels for the samples in the project and affix the labels to the outside of each container. The barcode label contains the following information:

- the project log number (e.g., S242450)
- the chain of custody (COC) designation for the different field samples (e.g., S242450-1, S242450-2, S242450-3, etc.) NOTE: This is not necessarily the same as the LIMS designation.
- the sample designation for each container for a particular field sample(e.g., S242450-1A, S242450-1B, S242450-2A, etc.)
- a barcode relating this information to the LIMS login

4.4 Distribution of Samples

After the samples have been inspected and accepted, distribute the samples to the appropriate department. The transfer of samples from the sample receipt personnel to the department is documented on the Sample Internal Custody Log (Figure 5). Interdivisional sample custody is documented on the Remote Division Sample Internal Custody Log (Figure 6).

4.5 Sample Receipt and Disposition in the Laboratory Departments

4.5.1 Inspect the samples to determine if the number and types of samples are consistent with the Sample Internal Custody Log. If the number and types of samples agree, sign the Log to indicate agreement. If there is a discrepancy, contact the department supervisor or laboratory manager and project manager or designee to resolve the discrepancy immediately. An anomaly form is used to document any problems at this point.

4.5.2 Log the samples into the department storage area using the barcode reader. Track the disposition of each sample using the barcode reader when:

- the sample is removed from the storage area
- the sample is returned from the storage area after use
- the sample container is empty
- the sample is removed from the storage area for disposal

5.0 RESPONSIBILITIES

5.1 The sample custodian (Custody Supervisor) is responsible for:

- supervision of custody technicians
- maintenance of chain-of-custody records
- identification, documentation, and project management notification of all non-conformances and anomalies associated with sample receipt
- identification and implementation all non-routine custody procedures

5.2 Custody personnel are responsible for:

- inspection of cooler condition and sample integrity
- unpacking field samples
- documentation of sample receipt into the laboratory
- distributing field samples to the appropriate laboratory

5.3 Project management personnel are responsible for

- notifying the client of non-conformances or anomalies associated with samples
- logging samples into the Laboratory Information Management System
- notifying custody personnel of client-specific or state/program-specific requirements such as the use of a cooler checklist, non-routine hold times, etc.

5.4 Laboratory personnel are responsible for

- receiving samples from custody personnel
- where applicable, checking the chemical preservative of the field samples
- properly storing the samples until the time of analysis
- documenting any non-conformances or anomalies and notifying the project manager or designee

6.0 REFERENCES

STL Quality Management Plan (QMP), current revision.

Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.

STL-8240 (0701)

SEVERN TRENT SERVICES

FIGURE 1

Serial Number 037919

SEVERN TRENT SERVICES

ANALYSIS REQUEST AND CHAIN OF CUSTODY RECORD

STL Savannah

◯ STL Savannah
5102 LaRoche Avenue
Savannah, GA 31404

Website: www.stl-inc.com
Phone: (912) 354-7858
Fax: (912) 352-0165

◯ Alternate Laboratory Name/Location

Phone:
Fax:

PROJECT REFERENCE	PROJECT NO.	PROJECT LOCATION (STATE)	MATRIX TYPE	REQUIRED ANALYSIS	PAGE	OF
STL (LAB) PROJECT MANAGER	P.O. NUMBER	CONTRACT NO.			STANDARD REPORT DELIVERY ◯ DATE DUE____	
CLIENT (SITE) PM	CLIENT PHONE	CLIENT FAX				
CLIENT NAME	CLIENT E-MAIL				EXPEDITED REPORT DELIVERY (SURCHARGE) ◯ DATE DUE____	
CLIENT ADDRESS						
COMPANY CONTRACTING THIS WORK (if applicable)				PRESERVATIVE	NUMBER OF COOLERS SUBMITTED PER SHIPMENT:	

Matrix type columns: COMPOSITE (C) OR GRAB (G) INDICATE; AQUEOUS (WATER); SOLID OR SEMISOLID; AIR; NONAQUEOUS LIQUID (OIL, SOLVENT, ...)

SAMPLE DATE	SAMPLE TIME	SAMPLE IDENTIFICATION	COMPOSITE (C) OR GRAB (G)	AQUEOUS (WATER)	SOLID OR SEMISOLID	AIR	NONAQUEOUS LIQUID	NUMBER OF CONTAINERS SUBMITTED										REMARKS

RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RELINQUISHED BY: (SIGNATURE)	DATE	TIME	RELINQUISHED BY: (SIGNATURE)	DATE	TIME
EMPTY CONTAINERS								
RECEIVED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME	RECEIVED BY: (SIGNATURE)	DATE	TIME
EMPTY CONTAINERS								

LABORATORY USE ONLY [illegible]

ORIGINAL – RETURN TO LABORATORY WITH SAMPLE(S)

FIGURE 2 - ANALYSIS WITH EXPEDITED HOLDING TIME		
Analysis	**Holding Time**	**Matrix**
MICROBIOLOGICAL PARAMETERS		
Fecal, Total Coliform (Environmental)	6 hours	Water
Fecal, Total Coliform (Drinking Water)	30 hours	Water
Heterotrophic Plate Count	6 hours	Water/Solid
Presence-Absence Coliform	6 hours	Water
MNO-MUG	6 hours	Water
GENERAL CHEMISTRY PARAMETERS		
BOD/CBOD (Biochemical Oxygen Demand)	48 hours	Water
Color	48 hours	Water
D.O. - Dissolved Oxygen	Do immediately	Water
Ferrous Iron (Fe^{2+})	24 hours	Water
Free Liquid 9095 Method (Paint Filter)	48 hours	Semi-solid
Hexavalent Chromium (Cr6+)	24 hours	Water
MBAS, surfactants	48 hours	Water
NO_2 – Nitrite	48 hours	Water
NO_3 – Nitrate	48 hours	Water
Odor	6 hours	Water
Oxidation Reduction Potential (ReDox or ORP)	Do immediately	Water/Solid
pH (hydrogen ion)	Do immediately	Water
PO_4, Orthophosphate	48 hours	Water
Reactivity (Releasable Sulfide/Releasable Cyanide)	As soon as possible	Water/Solid

FIGURE 2 - ANALYSIS WITH EXPEDITED HOLDING TIME		
Analysis	**Holding Time**	**Matrix**
GENERAL CHEMISTRY		
SC (Specific Conductivity)	24 hours	Water
Sulfide	7 days	Water
Sulfite	Do immediately	Water
TDS/TSS/TS (Total Dissolved Solids, Total Suspended Solids, Total Solids)	7 days	Water
Total Residual Chlorine	Do immediately	Water
Turbidity	48 hours	Water
METALS		
3030C Digestion (acid extractable)	72 hours	Water
Ferrous Iron (Fe^{2+})	24 hours	Water
Hexavalent Chromium (Cr6+)	24 hours	Water
HPLC (STL Tallahassee)		
Formaldehyde	72 hours	Water
AIR		
Tedlar Bags - EPA 18	72 hours	Air
VOLATILES		
Unpreserved VOC (no blue dot)	7 days	Water
603/8030 (Acrolein/Acrylonitrile)	3 days	Water

FIGURE 3

ANOMALY REPORT

Date: ___________ Log #: ____________ Sample ID: ____________ Client: ____________

Dept: ____ EX ____ GE ____ LC ____ ME ____ RA

____ CU ____ SG ____ SM ____ VG ____ VM ____ AI

Analysis: ____________ Reported by: __________

Anomaly:

☐ Sample matrix is different than indicated by log-in.

Logged in as	*Best described as*	
Water	*Water*	*Non-aqueous liquid*
Soil	*Soil*	*Sludge*
Oil	*Oil*	*Product*
	Other ____________________	

☐ Sample was received with inadequate preservation, and was preserved upon receipt.

☐ Sample received in an incompatible sample container. ____ *glass* ____ *plastic* ____ *other* __________

☐ MS/MSD failed while the LCS/LCSD passed criteria, for a drinking water parameter. Method indicates data qualification.

☐ Target analyte(s) detected in drinking water sample. (Describe below)

☐ Sample exhibits gross non-homogeneity. (Describe below)

☐ Insufficient sample received for analysis.

☐ Data qualifier needed. Discuss with DM/LM before reporting.

☐ Grand Mean exception was utilized for Initial Calibration (specify compounds). (SW-846 Only)

☐ Grand Mean exception was utilized for Continuing Calibration (specify compounds). (SW-846 Only)

Other ____

Custody: ***ALWAYS ATTACH A COPY OF COC WITH HIGHLIGHTED DEFICIENCY**

☐ Sample description discrepancy between COC & Container
☐ Custody seals broken
☐ Sample container breakage
☐ Incomplete COC
☐ Cooler temp >6°C or frozen
☐ Sample container partially filled
☐ Sample received not listed on COC
☐ Improperly preserved sample

Comments:

Client Notified: ☐Yes ☐No
Contact:

Date:

Resolution:

Route to:

Project Manager: ______________________________

STL Facility: Savannah________ Mobile________ Tampa West________ Tallahassee________

FIGURE 4

SAMPLE REGISTRY

LOG NO.	TIME RECEIVED	DATE RECEIVED	DELIVERED BY	CLIENT ID	NUMBER OF COOLERS RECEIVED	INITIATE ANOMALLY? Y/N	CONTAINER TEMPERATURE CORRECT	ADDITIONAL SAMPLE INFORMATION

FIGURE 5

STL SAVANNAH										
STL SAVANNAH LOG NUMBER ______________										
CLIENT______________				COURIER__________				LARGE HARD COOLERS _____		
# COOLERS/CLIENT______________				COOLER TEMPERATURE_______				SMALL/MED COOLERS _____		
GENERAL BOTTLES	P	#	METALS BOTTLES	P	#	VOLATILE BOTTLES	P	#	EXTRACTION BOTTLES	P	#
LIQUID			**LIQUID**			**LIQUID**			**LIQUID**		
500 amb glass			500 m/m nalgene			40 ml vial			Ltr n/m amb glass		
250 amb glass			500 m/m nalgene			40 ml vial			Ltr w/m amb glass		
125 amb glass			250 m/m nalgene			**SOIL**			500 m/m amb glass		
Ltr m/m nalgene			250 m/m nalgene			40 ml vial			250 m/m amb glass		
500 m/m nalgene			125 m/m nalgene			Encore splers/25g			500 m/m nalgene		
250 m/m nalgene			**SOIL**			Encore splers/5g			250 m/m nalgene		
250 m/m nalgene			Ltr w/m plastic			125 clr w/m septa			125 m/m nalgene		
250 m/m nalgene			500 w/m plastic			125 amb w/m			**SOIL**		
125 m/m nalgene			250 w/m plastic			**AIR**			500 w/m glass		
DO bottle			**OTHER**			Tedlar bags			250 w/m glass		
SOIL						Vacuum cans			125 w/m amb glass		
250 m/m nalgene						**OTHER**			500 w/m plastic		
OTHER									250 w/m plastic		
									OTHER		
VERIFY AMOUNT			**VERIFY AMOUNT**			**VERIFY AMOUNT**			**VERIFY AMOUNT**		
TOTAL CONTAINERS			**TOTAL CONTAINERS**			**TOTAL CONTAINERS**			**TOTAL CONTAINERS**		
SAMPLE TRANSFER INFORMATION:											
CUSTODY INITIAL/DATE			**CUSTODY INITIAL/DATE**			**CUSTODY INITIAL/DATE**			**CUSTODY INITIAL/DATE**		
GENERAL INITIALS/DATE			**METALS INITIAL/DATE**			**VOLATILES INITIAL/DATE**			**EXTRACTION INITIAL DATE**		
MISC BOTTLES STORED IN REFRIGERATOR FOR SUB-CONTRACTOR/REMOTE TRANSFER											

FIGURE 6

REMOTE DIVISION

SAMPLE INTERNAL CUSTODY LOG

STL FACILITY: ____________________

 # COOLERS ____________________

TEMPERATURE(S) ____________________

LOG# FOR GENERAL LAB	#	LOG# FOR METALS LAB	#	LOG# FOR VOLATILES LAB	#	LOG# FOR EXTRACTION LAB	#
PLEASE VERIFY ✓		PLEASE VERIFY ✓		PLEASE VERIFY ✓		PLEASE VERIFY ✓	
TOTAL CONTAINERS		TOTAL CONTAINERS		TOTAL CONTAINERS		TOTAL CONTAINERS	

RELINQUISHED INFORMATION:

CUSTODY INITIAL/DATE **CUSTODY** INITIAL/DATE **CUSTODY** INITIAL/DATE **CUSTODY** INITIAL/DATE

____________________ ____________________ ____________________ ____________________

GENERAL INITIAL/DATE **METALS** INITIAL/DATE **VOLATILES** INITIAL/DATE **EXTRACTION** INITIAL/DATE

FCU027:06.19.01:2

INTERNAL CHAIN-OF CUSTODY

Approved by:

R. Wayne Robb ____________ Date 15 Aug 2001

Title: Technical Manager, QA

STL ~~Savannah~~ Tallahassee Mobile Tampa West

1.0 SCOPE AND APPLICATION

This SOP describes the procedures used for the distribution and tracking of samples that require a more detailed level of custody than described in STL SOP CU01:*Receipt, Log Number Assignment, and Distribution of Field Samples.*

2.0 SUMMARY OF METHOD

Upon arrival in the lab, the shipping containers are opened and inspected according to the procedures described in STL SOP CU01. A sample tracking label is affixed to each sample container and the samples are distributed to the appropriate laboratory department. The samples are relinquished to the department, and if required, the samples are checked by departmental analysts for proper preservation. The sample is then properly stored until preparation and/or analysis. Documentation is provided on the sample tracking label, sample preparation logs, the internal chain-of-custody logs, and the sample/waste disposal logs. The sample tracking labels and section internal chain-of-custody logs are maintained in department-specific notebooks.

3.0 PROCEDURE

3.1 Initiation of Internal Custody-Custody Department Personnel

3.1.1 Log samples into the lab using the procedures described in STL SOP CU01.

3.1.2 After samples are received and documented, use the LIMS to print out sample labels for each sample container. It is important that each sample have its own label. The sample log number, client ID, sample ID, and sample location items should be completed at this time.

3.1.3 Write an alpha character on the label and on the sample container to uniquely identify the container. For example, if six 1-L containers are submitted for sample MW-1, one container is designated A, another B, and so forth, with the last container designated F. See Table 1 for examples of the label and the labeling method.

3.1.4 Attach the label to the appropriate sample and distribute the samples to the departments in accordance with Section 3.5 of STL SOP CU01. The Sample Internal Custody Log (STL SOP CU01, Figure 5) is used to document the transfer of the samples from the receiving department to the analytical departments (EX, ME, VM/VG, etc.).

3.2 LIMS Log-in Status and Worksheets-Project Managers and Assistants

Samples that require a higher level of internal chain-of-custody documentation will be designated by an I status code in the LIMS. The work for these samples will be flagged on every LIMS-generated worksheet and status sheet.

3.3 Sample Chain-of Custody-Department Custody Personnel and Analysts

3.3.1 The Sample Internal Custody Log (STL SOP CU01, Figure 5) is signed by the analytical department custody personnel. This log is the initial documentation for receiving the samples into the department.

2.1.1 If required, check the sample preservation and document as described in the appropriate analytical SOP. Transfer the samples to the designated storage area.

3.3.3 When the sample is removed from the storage area, write the date and time that the sample was removed and initial the sample label. For example, if the sample was removed on June 6, 1998 at 10:00am by WR, the label will be documented :

Log Number: S880001
Client: Alpha Industries
Sample ID: MW-1 A

LOCATION: EX

OUT: **6/6/98 10a.m. WR** IN:

OUT: IN:

OUT: IN:

OUT: IN:

EMPTY:

DISPOSAL:

2.1.2 If the sample is returned to the storage area, write the date and time that the sample was returned on the sample label and initial the label. For example, if the sample was returned on June 6, 1998, at 11:10am by WR, the label will be documented :

Log Number: S880001
Client: Alpha Industries
Sample ID: MW-1 A

LOCATION: EX

OUT: 6/6/98 10:00a.m. WR IN: **6/6/98 11:10am WR**

OUT: IN:

OUT: IN:

OUT: IN:

EMPTY:

DISPOSAL:

3.3.5 After the entire contents of the sample container has been used, write the date on the sample label beside EMPTY and initial the label.

Log Number: S880001 Client: Alpha Industries Sample ID: MW-1 B	
LOCATION: EX	
OUT: 6/6/98 10:00a.m. WR	IN:
OUT:	IN:
OUT:	IN:
OUT:	IN:
EMPTY: **6/6/98 WR**	
DISPOSAL:	

If the container is used for multiple analyses, the label may have several OUT/IN dates, times, and initials before the sample is depleted. Transfer the label to the department notebook designated for the maintaining the labels and dispose of the sample container.

3.3.6 If the sample container has not been used for analysis or if sample remains in the container, write the date that the sample was removed from the storage area for disposal on the sample label and initial the label. Transfer the sample to the designated area for disposal.

Log Number: S880001 Client: Alpha Industries Sample ID: MW-1 F	
LOCATION: EX	
OUT:	IN:
OUT:	IN:
OUT:	IN:
OUT:	IN:
EMPTY:	
DISPOSAL: **06/21/98 WR**	

2.2 Extracts and Leachates

Metals and general lab digestates are not tracked since refrigeration is not required. The digestion matrix is stable and not prone to evaporation or degradation if analyzed within the recommended hold times.

3.4.1 If internal custody is required for TCLP or other leachates that will not be analyzed on the same day as the leaching procedure or filtration step, the procedures described for field samples are employed. A sample label is affixed to the storage container to track the sample from the leaching procedure through the final preparation (extraction or digestion).

NOTE: If a leachate must be retained for multiple analyses over several days, a sample label must be used.

3.4.2 Internal custody of extracts will be tracked on the form given in Table 2. Each time an extract is removed from the designated storage refrigerator, the date and time of removal must be recorded and initialed.
If the extract is returned to the storage refrigerator, the date and time of return is recorded and initialed.

The internal chain-of custody forms are retained in the prep or analytical sections (VG/VM, EX, GE, etc.) in designated notebooks. The forms are filed by batch number and sample identification.

Table 1-Example of Labels for a Sample With Multiple Containers of the Same Type

Log Number: S880001 Client: Alpha Industries *Sample ID: MW-1 A* LOCATION: EX OUT: IN: OUT: IN: OUT: IN: EMPTY: DISPOSAL:	Log Number: S880001 Client: Alpha Industries *Sample ID: MW-1 B* LOCATION: EX OUT: IN: OUT: IN: OUT: IN: EMPTY: DISPOSAL:
Log Number: S880001 Client: Alpha Industries Sample ID: MW-1 C LOCATION: EX OUT: IN: OUT: IN: OUT: IN: EMPTY: DISPOSAL:	Log Number: S880001 Client: Alpha Industries Sample ID: MW-1 D LOCATION: EX OUT: IN: OUT: IN: OUT: IN: EMPTY: DISPOSAL:
Log Number: S880001 Client: Alpha Industries Sample ID: MW-1 E LOCATION: EX OUT: IN: OUT: IN: OUT: IN: EMPTY: DISPOSAL:	Log Number: S880001 Client: Alpha Industries Sample ID: MW-1 F LOCATION: EX OUT: IN: OUT: IN: OUT: IN: EMPTY: DISPOSAL:

SEVERN TRENT SERVICES

PROCEDURE FOR CONTAMINANT-FREE SAMPLE CONTAINERS

Approved by: R. Wayne Robbins 16 Aug 2001
Date

Title: Technical Manager, QA

STL ✓ Savannah Tallahassee ✓ Mobile Tampa West

1.0 OBJECTIVES AND SCOPE

This SOP describes STL's procedure for testing and verifying the cleaning of sample containers.

Most environmental sampling and analytical procedures offer various opportunities for sample contamination. The sample container itself represents one potential source of sample contamination. Therefore, it is important that STL's pre-cleaned sample containers meet strict, documented acceptance criteria to ensure container contamination does not affect analytical results. In all cases STL's acceptance criteria for sample containers meets or exceeds guidelines established by the EPA as well as the industry standard (I-Chem Level III) criteria.

2.0 SUMMARY OF METHOD

Sampling containers (Tables 1) are pre-cleaned by the STL approved vendor. Prior to introduction of containers into the laboratory network, each lot of container is tested for contamination. The analyses performed on each type of container are given in Tables 1 and 2. Containers for inorganic analytes and volatiles are filled with reagent water and, if required by the procedure, a preservative is added. The container is allowed to "leach" for a specified period of time and is then tested by the referenced procedure. Containers for semivolatile organic parameters are rinsed with a suitable solvent. The solvent is concentrated and analyzed by the referenced procedure.

A container lot is accepted if the target analyte concentrations are less than 1/4 the RL specified in the current STL quality assurance plans. The data for each analysis are reported as ND (not detected) if the results are less than 1/4 the RL published in the current revision of the STL CQAP.

3.0 PROCEDURE

3.1 Sample Container Specifications

STL recommended container types and sizes for each analysis are listed in Table 1. All glass and plastic containers are purchased pre-cleaned from a STL approved vendor. The cleaning procedures are designed to exceed EPA recommended procedures and to meet STL's sample container criteria.

3.2 Contaminant Level Specifications

Acceptance criteria for containers are based on 1/4 the RL listed in STL QAPP (Section 5). These acceptance criteria are in all cases lower than EPA specifications for maximum contamination.

3.3 Sample Container Testing and Documentation Procedures

3.3.1 *Quality Assurance of Containers*

The objectives of this Section are to present procedures for evaluating data to ensure that specifications identified in Section II have been met; and discuss techniques for the acceptance criteria analysis of sample containers.

Documentation indicating that the container lot has passed all acceptance criteria requirements are kept by STL for each container lot. Each Report of Analysis for sample containers is kept in the STL LIMS and is signed by the Lab Manager, QA Manager or QA Officer, or the project manager of the lab performing the container certification. The report includes a statement affirming that all acceptance criteria were met. Copies of raw data from applicable analyses of the sample containers are kept. Original documentation is retained for at least 3 years. Minimum documentation that should be available, if applicable, for each lot of containers includes:

- A statement that "Sample container lot ______ meets or exceeds all acceptance criteria established in 'Specifications and Guidance for Contaminant-Free Sample Containers;'"
- Reconstructed Ion Chromatographs (RICs) from volatile and semivolatile organics determinations, including calibration standards, check samples, and blanks;
- GC chromatographs from pesticides determinations, including calibration verification standards, check samples, and blanks;
- ICP instrument readouts from metals determinations, including calibration verification standards, check samples, and blanks;
- General Chemistry raw data sheets and instrument readouts from these determinations, including calibration verification standards, check samples, and blanks.

3.3.2 Quality Control Inspection of Cleaned Lots of Containers

Following container cleaning and labeling, a minimum of three containers should be randomly selected from each container lot to be used for QC purposes. The containers are assigned an STL log number that is the same as the container lot number.

All container certification are logged into the STL LIMS using a unique container client code. This allows access to the results of the container certification to each laboratory in the STL network. The following statement is added to each report:

> "Sample container lot ______________meets or exceeds all acceptance criteria established in "Specifications and Guidance for Contaminant-free Containers."

If the Analytical QC Containers pass the acceptance criteria, the data are approved by the production supervisor or technical manager, the LIMS Report of Analysis is signed by the container certification project manager, and the appropriate QC number is entered in the preparation/QC log to release the lot for shipment to clients. (Figure 1-Custody Sample Container Lot Tracking Form)

If the Analytical QC Containers are found to be contaminated, the lot must be rejected. Excessive QC rejection for a particular container type should be noted for future reference. Review of data (by Technical Manager) should include a flag for any results that appear anomolous. Rerun analysis if data are questionable.

A laboratory control sample (LCS) and a method or reagent blank should be prepared and analyzed with each container QC analysis. All container QC analysis are identified by the bottle type, lot number, and the date of analysis. The data is stored in a central QC file.

A container lot should not be released for shipment prior to QC analysis and clearance. Once the containers have passed QC inspection, the containers should be stored in a contaminant-free area until packaging and shipment.

3.4 Quality Control Analysis

The types of QC analyses correlate with the type of containers being analyzed and their future use in sample collection. QC analyses should be performed according to the container type and related sample type and utilize the specific method(s) described below. The results are based on the routine volume or weight of sample utilized for the analysis and are compared to 1/4 the STL RL for that parameter. For inorganic soil parameters: if the routine weight is 1g, use 1mL of the leachate; if the routine weight is 10g, use 10mL of the leachate.

If the results are less that the MDL, report as "ND"-not detected.

3.4.1. Determination of Semivolatile Organics, Pesticides, Herbicides, and Other Extractable Organics

3.4.1.1 Semivolatile Organic Sample Container Preparation and Analysis (GC/MS 8270)

- Add 60mL of residue-grade methylene chloride to each container and shake for two minutes.
- Transfer the solvent to a Zymark tube and evaporate each extract to 1.0mL.
- Analyze the extract by SW-846 Method 8270 (STL SOP SM05). In addition, a library search is performed to determine if non-target compounds are present in the extract. The tentatively identified compounds(TICs) are reported if detected.

3.4.1.2 Chlorinated and Organophosphorous Pesticide Sample Container Preparation and Analysis (GC/Electron Capture and GC/NPD)

- Add 60mL of residue-grade methylene chloride to each container and shake for two minutes.
- Transfer the solvent to a Zymark tube and evaporate each extract to 1.0mL.
- Add 50mL of residue-grade hexane to the Zymark tube. Concentrate to less than 10mL to completely evaporate the methylene chloride. Bring the extract to a final volume of 10mL with hexane.
- Split the extract into two 5mL aliquots.
- Analyze one aliquot of the extract by SW-846 Method 8080 (STL SOP SG45).
- Analyze the other aliquot of the extract by SW-846 Method 8141 (STL SOP SG50).

3.1.4.3 Chlorinated Herbicides Sample Container Preparation and Analysis (GC/Electron Capture)

- Add 60-mL of residue-grade methanol to each container and shake for two minutes.
- Transfer the solvent to a Zymark tube and evaporate to 1.0mL.
- Add 9mL of diethyl ether and perform the diazomethane esterification (see STL SOP EX45 for esterification and extract prep).
- Analyze the extract by SW-846 Method 8151 (STL SOP SG65).

3.4.1.4 Other GC, GC/MS, and HPLC Methods

- The remainder of the extractable organic analytes are performed on the extract by an appropriate GC, GC/MS, and LC methods listed in the STL QAP (Section 5).

3.4.2 Determination of Volatile Organics

- Add 1:1 HCl preservative to each container
- Fill the VOA vials with volatile free water and cap the container with zero headspace.
- Transfer the vials to the volatiles storage area at 4C± 2C for 48 hours.
- Analyze 25mL of water in each vial by SW-846 Method 8260 (STL SOP VM20).
- All analysis, calibrations, and QC should be performed as described in the latest STL SOP on Method 8260 (25 ml purge). Results are reported down to 1/4 the STL RL. A GC/MS library search is also performed and all TICs are reported.

3.4.3 Metals Sample Containers Preparation and Analysis

- Fill the containers with reagent water and acidify with reagent-grade HNO3 to pH <2. Cap and shake for three to five minutes.
- Allow the container to stand at room temperature for 48 hours.
- Analyze the undigested water using the recent Trace ICP Method 6010 and Mercury Method 7470. Results are reported down to 1/4 the STL RL.

3.4.4 Cyanide Containers Preparation and Analysis

- Fill the container with reagent water and add appropriate preservative. Cap the container and shake vigorously for two minutes.
- All analysis, calibrations, and QC should be performed as described in the most recent STL SOP. Data are reported to 1/4 the STL RL.

3.4.5 Wet Chemistry Sample Containers Preparation and Analysis

- Fill container with reagent water in the container. Add the appropriate preservative, cap the container and shake vigorously for two minutes.
- All analysis, calibrations, and QC should be performed as described in the most recent STL SOP for each wet chemistry analysis. Data are reported down to 1/4 the STL RL.

3.5 Container Tracking

The Custody Sample Container Lot Tracking Form (Figure 1) is used to track the containers that are used over a given period of time. A container lot is not introduced into the STL network for use in sampling until all QC tests are completed.

Table 1-LIQUIDS

Parameter	Sample Container	Part Number	Method of Certification
Microbiology			
Coliform, fecal & total	2 x 100-ml sterile	66175-105	By Vendor
Fecal Streptococci	2 x 100-ml sterile	66175-105	By Vendor
Plate Count	2 x 100-ml sterile	66175-105	By Vendor
Inorganic Tests			
Acidity	250-ml P	SAV-214	305.1
Alkalinity	120-ml P	BPC 3125	310.1
Ammonia	120-ml P	BPC 3125	350.1
BOD	500-ml P	SAV-112	405.1/SM5210B
Bromide	120-ml P	BPC 3125	300.0
COD	120-ml P	BPC 3125	410.2
Chloride	120-ml P	BPC 3125	325.2
Cyanide, total and amenable	250-ml P	SAV-214	9012 w/autodistillation
Fluoride	120-ml P	BPC 3125	300.0/340.2
Hardness	250-ml P	SAV-214	130.2
Hydrogen ion	120-ml P	BPC 3125	150.1
Kjeldahl and organic nitrogen	250-ml P	SAV-214	351.2
Chromium VI	250-ml P	SAV-214	7196
Mercury	250-ml P	SAV-214	7470/7471
Metals, except Chromium VI and Mercury	250 ml P	SAV-214	6010-Trace
Nitrate – Nitrite	120-ml P	BPC3125	353.2
Organic Carbon	125-ml amb G	APC 1260	415.1
Orthophosphate	120-ml P	BPC 3125	365.2
Phosphorus, total	120-ml P	BPC 3125	365.4
Residue, total	500-ml P	SAV-112	160.1
Silica	250-ml P	SAV-214	6010
Specific Conductance	120-ml P	BPC 3125	120.1
Sulfate	120-ml P	BPC 3125	300.0
Sulfide	500-ml P	SAV-112	376.2
Sulfite	120-ml P	BPC 3125	377.1
Surfactants	500-ml P	SAV-112	425.1
Turbidity	120-ml P	BPC 3125	180.1

Table 1

Organic Tests:	Sample Container	Part Number	Method of Certification
Chlorinated Herbicides	2 X 1-L amb G	273632	8151
Purgeable Halocarbons	3 X 40-ml G	SAV-89	8260
Purgeable Aromatic Hydrocarbons	3 X 40-ml G	SAV-89	8260
Phenols	2 X 1-L amb G	273632	8270
Benzidines	2 X 1-L amb G	273632	8270
Phthalate esters	2 X 1-L amb G	273632	8270
Nitrosamines	2 X 1-L amb G	273632	no
Pesticides	2 X 1-L amb G	273632	8081
PCBs	2 X 1-L amb G	273632	8082
PAHs	2 X 1-L amb G	273632	8270
Chlorinated hydrocarbons	2 X 1-L amb G	273632	8270
Total organic halogens	500-ml amb G	APC 3220	450.1
Phenols, total recoverable	500-ml amb G	APC 3220	420.1/9065
Oil and Grease	500mL or 1-L	APC 3220/ APC 1040	413.2/ By Vendor

Table 1-SOILS

Soils:	Sample Container	Part Number	Method of Certification
Cyanide	250-ml P	BPC 3700	9012
Sulfide	250-ml P	BPC 3700	376.2
Phenols, Total Recoverable (Savannah Only)	125-ml amb G	APC 1260	By Vendor
Nutrients	250-ml P	BPC 3700	350.1/300.0 325.2/353.2/ 351.2/365.2/ 365.4
TOC	125-ml amb G	APC 1260	By Vendor
Metals (except Mercury)	250-ml P	BPC 3700	6010 – Trace
Semivolatile Organics	250-ml G	270808	8270/8081/ 8141/8150
(Multiple Methods)	500-ml G	270816	8270/8081/ 8141/8151
Volatile Organics	125-ml amb G	APC 1261	By Vendor
Mercury	250-ml P	BPC 3700	7471

Table 2

Container: 120mL Plastic
Part Number: BPC 3125

General Lab Parameters

Unpreserved Containers:	Alkalinity (310.1) Bromide (300.0) Chloride (325.2) Fluoride (300.0) ortho-phosphate (365.2) pH (150.1) Specific Conductance (120.1) Sulfate (300.0) Sulfite (377.1) Turbidity (180.1)
Preserved with H2SO4:	Ammonia (350.1) COD (410.2 or SM 5220C) Nitrate/Nitrite (353.2) TKN (351.2) Total Phosphorus (365.4)
Preserved with HNO3:	Metals (6010) Mercury (7470)

Container: 250mL Plastic
Part Number: SAV-214

General Lab Parameters

Unpreserved container:	Acidity (305.1) Hexavalent chromium (7196)
Preserved with H2SO4:	TKN(351.2)
Preserved with NaOH:	Cyanide – Total (9012)

Metals Lab Parameters

Preserved with HNO3:	ICP-Trace (6010-Trace) Mercury (7470/7471) Silica (6010) Hardness (130.2)

Table 2

Container: 500mL Plastic
Part Number: SAV-112

General Chemistry Parameters

Unpreserved container: BOD (405.1)
Surfactants (425.1)
Total residue (160.1)

Preserved with ZnAc: Sulfide (376.2)

Preserved with HNO3: Metals (6010-Trace)
Mercury (7470/7471)

Container: 40mL Glass with Teflon-lined SeptumCap
Part Number: SAV-89

VM/VG Parameters

Preserved with HCl: Volatiles (8260-25mL purge)

Container: 500mL Amber Glass
Part Number: APC 3220

General Chemistry Parameter

Preserved with H2SO4: Oil & Grease (413.2)
TOX (9020)
Total Recoverable Phenolics (420.1)

Container: 125mL Amber Glass with Teflon Septum Cap
Part Number: APC 1261

VG/VM Parameters

Unpreserved (SS): VOC by 8260

Container: 125 mL Amber Glass
Part Number: APC 1260

General Chemistry Parameters

Unpreserved (SS): Total Recoverable Phenolics (420.1)
TOC (415.1)
TPH (418.1)

Preserved with HCl (liquids): TPH (418.1)

Table 2

Container: 1-L Amber Glass
Part Number: 273632

SM/SG Parameters

Unpreserved container:
Herbicides (8151)
BNA (8270)
Pesticides/PCBs (8080)
Phos. Pesticides (8141)

Container: 250mL Plastic Wide Mouth
Part Number: BPC 3700

General Chemistry Parameters

Unpreserved container:
Cyanide-SS (9012)
Sulfide-SS (9030)
Ammonia-SS (350.1)*
IC-SS (300.0)
Chloride-SS (325.2)
Nitrate/Nitrite-SS (353.2)
TKN-SS (351.2)
o-Phosphate-SS (365.2)
Total Phosphorus-SS (365.4)
Sulfate-SS (300.0)

*ammonia extracted with KCl solution

Metals Lab Parameters

Unpreserved container:
Metals-SS (6010-Trace)
Mercury -SS (7471)

Container: 250mL Glass
Part Number: 270808

SG/SM Parameter

Unpreserved container:
BNA-SS (8270)
Pesticides/PCBs-SS (8081)
Phos. Pesticides-SS (8141)
Chlorinated Herbicides-SS (8151)

FIGURE 1

CUSTODY SAMPLE CONTAINER LOT TRACKING FORM

BOTTLE TYPE____________________________

DATE REC'D	LOT NUMBER	# CASES REC'D	START DATE*	INITIAL BOTTLE ORDER ID #	STOP DATE*	FINAL BOTTLE ORDER ID #

* IF START DATE FOR NEXT LOT OF BOTTLES IS DIFFERENT THAN THE PREVIOUS BOTTLES STOP DATE, THEN IT IS NOT NECESSARY TO USE THE BOTTLE ORDER ID NUMBERS (USE N/A).

SEVERN TRENT STL

SEMI-VOLATILE COMPOUNDS BY GC/MS
Method: 8270C

Approved by:

R. Wayne Robbins — 30 Aug 2002
R. Wayne Robbins — Date

Title: Technical Manager

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This method can be used to determine the concentration of various semi-volatile organic compounds (SVOC) in groundwater, TCLP and SPLP leachates, soils, sediments, wastes, and solid sample extracts. The attached quantitation report (Appendix B) lists the routine target compounds, the retention times of the target compounds, the characteristic ions of the target compounds, and the internal standard associated with each target compound.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits for the target compounds are given in Section 5 of the current revision of the Laboratory Quality Manual (LQM).

2.0 SUMMARY OF METHOD

2.1 A measured volume or weight of sample is extracted using an appropriate extraction procedure. The extract is dried, concentrated to a volume of 1.0mL, and analyzed by GC/MS. Qualitative identification of the target compounds in the extract is based on the retention time and the mass spectra determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 This procedure is based on the guidance provided in SW-846 Method 8270C.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The toxicity or carcinogenicity of each chemical used in this method has not been precisely defined. Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, and lab glasses or face shield should be worn while handling extracts and standards. Standard preparation, addition of the internal standard solution, and sample extract dilution should be performed in a hood or well ventilated area.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst. These sheets specify the type of hazard that each chemical poses and the procedures that are used to handle these materials safely.

3.4 The exit vent of the splitless injector must have a carbon trap in-line to collect the semivolatile compounds that are vented during the injection of the extract. The traps should be changed every six months and disposed of in accordance with SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 Method interferences may be caused by contaminants in solvents, reagents, or glassware. Glassware and/or extraction vessels that have not been properly cleaned may contribute artifacts that make identification and quantification of the target compounds difficult. Elevated baselines may be due to oils, greases, or other hydrocarbons that may be extracted from improperly cleaned glassware or extraction vessels.

4.2 Matrix interferences may be caused by contaminants that are extracted from the sample matrix. The sample may require cleanup or dilution prior to analysis to reduce or eliminate the interferences. Sample extracts that contain high concentrations of non-volatile material such as lipids and high molecular weight resins and polymers may require the optional GPC cleanup prior to analysis. The GPC cleanup is generally not effective in removing non-target material that is associated with common petroleum products like diesel.

4.3 Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days from TCLP leaching procedure	40 days

Refrigerator temperature acceptance criterion is less than 6C with no frozen samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph- Hewlett-Packard (HP) 5890 or equivalent with compatible autosampler, splitless injector, and direct capillary interface. The exit vent of the splitless injector must have a carbon trap in-line to collect the semivolatile compounds that are vented during the injection of extracts. The carbon traps should be changed every six months.

6.2 Mass spectrometer- HP5971, HP5972, HP5973 or equivalent

6.3 Recommended Capillary column-HP-5MS, 30m x 0.25mm ID x 0.25um film thickness or equivalent column

6.4 Data system- compatible with GC/MS system

6.5 Microsyringes- appropriate volumes

6.6 Volumetric flasks- Class A, appropriate volumes

6.7 Autosampler vials and crimper- compatible with autosampler

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability.*

7.1 Methylene chloride- pesticide residue grade, for preparation of standards

7.2 Acetone- pesticide residue grade, for preparation of standards

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation.*

The lab should purchase certified solutions from STL approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation from neat materials.

8.1 Preparation of the Stocks from Neat Standards

The steps for the preparation of primary stock standards from neat materials are given in SOP *AN43: Standard Preparation.* The standards should be prepared in methylene chloride but may require other solvents to dissolve the material.

8.2 Preparation the calibration standards from the stock standards

A minimum of five calibration standards are prepared. The concentrations of the stock standards are in the 1000-10000ug/mL range. The recommended standards are listed in Section 10.2. The lowest level standard should be at the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve. Internal standards should be added to each standard to give a final concentration of 40ug/mL.

Each lab should develop controlled recipes that can be posted or maintained in appropriate logbooks.

9.0 SAMPLE PREPARATION

9.1 The sample extraction procedures are given in the following SOPs:

Matrix	SOP	Extraction Technique
Aqueous, TCLP leachates	EX30	Continuous Liquid-liquid Extraction
Aqueous, TCLP leachates	EX35	Separatory Funnel
Soils/Sediments	EX40	Sonication
Wastes	EX42	Waste dilution

9.2 The sample concentration procedures are given in SOP EX 50: Zymark Nitrogen Concentration.

9.3 Gel permeation chromatography (SOP EX61) may help to eliminate or minimize matrix interferences in a limited number of samples. The GPC cleanup is generally not effective on samples containing petroleum products.

10.0 PROCEDURE

10.1 Instrument Conditions

Instrument conditions may vary according to the sensitivity of each instrument. The following conditions are provided for guidance. The lab must optimize and document the conditions used for the analysis of SVOC by GC/MS.

Recommended Column:
HP-5MS 30m x 0.25mm ID x 0.25um film thickness or equivalent

Column flow: Approximately 1mL/min helium

GC Oven temperatures:
Initial column temperature: 45 C for 3 minutes
Column temperature program: 10C per minute
Final column temperature: 300C (until at least one minute past the elution time of Benzo (g,h,i) perylene).

GC injector parameters
Injector temperature: 250-270EC
Injection type: split, approximately 1:10 or splitless injection
Injector liner: 4mm ID quartz or 4mm glass, deactivated (single "Gooseneck")
Sample injection volume: 1-2uL

Mass Spectrometer and interface parameters
Mass spectrometer interface: 300C
Mass spectrometer source temperature: Factory Set
Mass range: 35-500amu, with a scan time of 1.0 scans per second or greater

10.2 Calibration

A minimum of five calibration standards are prepared and analyzed. The recommended standards are 10, 20, 50, 80, 100, 200ug/mL. The lowest level standard should be at or below the equivalent of the reporting limit and the rest of the standards should define the working range of the detector. Note that six calibration levels are required for a second order regression curve.

10.2.1 Fifty nanograms of DFTPP must be analyzed at the beginning of each 12-hour clock as a check on the "tune" of the mass spectrometer. Meeting the tuning criteria demonstrates that the instrument is measuring the proper masses in the proper ratios. The DFTPP analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of DFTPP. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage.

10.2.1.1 Prepare a 50ng/uL solution of tune/column evaluation standard containing each of the following compounds at 50ug/mL in methylene chloride: DFTPP, pentachlorophenol, p,p'-DDT, and benzidine.

10.2.1.2 Analyze a 1uL aliquot of the tune/column evaluation solution.

10.2.1.3 Evaluate the DFTPP peak.

-The chromatogram should exhibit acceptable baseline behavior and the DFTPP peak should be symmetrical.

-The spectrum of the DFTPP must meet the criteria listed in the SOP Summary (Appendix A). Background subtraction must be straightforward, that is, no scan within the elution window of DFTPP may be subtracted from another scan within the elution window, and designed only to eliminate column bleed or instrumental background. Scans +/- 2 scans from the apex can be evaluated for the DFTPP criteria. Consecutive scans within this range may be averaged to meet the criteria.

NOTE: The DFTPP analysis should be evaluated as to the relative size of the DFTPP peak under the m/z 198 profile. A benchmark area window should be established for each instrument and data system. Area outside of this window suggests instrumental problems such as a bad injection, clogged autosampler syringe, leaking injector, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open, etc.

If the DFTPP fails to meet the criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the DFTPP analysis, other corrective measures may include remaking the DFTPP standard, cleaning the mass spectrometer source, etc.

10.2.1.4 Benzidine and pentachlorophenol should be present at their normal responses with minimal peak tailing visible. Peak tailing guidance is taken from EPA Method 625 which allows pentachlorophenol to be less than or equal to five and benzidine less than or equal to three. Refer to Figure 1for an example of [eak tailing factor calculation.

This is a good check on the system: if pentachlorophenol (a CCC) does not respond well, the calibration standard should not be analyzed. Injector port and column maintenance should be performed and the tune/column evaluation standard reanalyzed.

The percent breakdown of p,p'- DDT is calculated using the following equation. The percent breakdown should not exceed 20%.

$$\%Breakdown = \frac{(areaDDE + areaDDD)}{(areaDDT + areaDDE + areaDDD)} x\ 100$$

Areas from the total ion chromatogram are used to calculate DDT breakdown.

10.2.2 After the DFTPP criteria and column evaluation criteria have been met, the initial calibration standards are analyzed.

10.2.2.1 Prepare the initial calibration standards. The lowest calibration standard should be at the RL and the rest of the standards will define the working range. See section 10.2 for guidance regarding calibration levels.

10.2.2.2 Set up a sequence and analyze the calibration standards. The injection volume must be the same for the calibration standards and all sample extracts.

10.2.3 Identify the internal standards, surrogates, and the target compounds. The data system must be updated with the proper retention times and ion data.

10.2.4 Calculate the relative response factor for each compound as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured
(See the attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration of the compound being measured (ug/mL)
Cis = concentration of the internal standard (40ug/mL)

Secondary ions may be used for quantification if there is interference with the primary quantitation ion. If a secondary ion is used for quantification, the concentration/response relationship of the secondary ion must be established. The secondary ion must meet the same calibration criteria as the primary ion.

10.2.5 Calculate the average relative response factor (RRF_{avg}) for each target compound and each surrogate compound:

$$RRF_{avg} = \frac{RRF1 + RRF2 + RRF3 .... + RRFn}{n}$$

RRF1 = relative response factor of the first standard
RRFn = relative response factor of the last standard
n = number of calibration standards

10.2.6 Calculate the standard deviation (SD) for the initial calibration standards:

$$SD = \sqrt{\sum_{i-1}^{n_1} \frac{(RRF_i - RRF_{avg})^2}{n-1}}$$

10.2.7 Calculate the relative standard deviation (%RSD) of the target compounds in the calibration standards.

$$\%RSD = \frac{SD}{RRF_{avg}} x\, 100$$

10.2.8 Evaluation of the Initial Calibration

The initial calibration is evaluated specifically for the calibration check compounds (CCC) and the system performance check compounds (SPCC). The CCC and SPCC criteria are given in the SOP Summary (Appendix A). The %RSD criteria for CCC and minimum RRF for SPCC must be met before the analysis of sample extracts can begin.

If the CCC and SPCC criteria are not met, action must be taken to bring the analytical system into compliance with the criteria. This action may include injection port maintenance, source cleaning, changing the column, or replacement of injection port lines and assembly. In any case, if the criteria are not met, the initial calibration must be repeated. The analyst must be aware of the 12-hour clock for the DFTPP analysis. The DFTPP criteria must be met prior to the analysis of the calibration standards.

10.2.9 After the initial calibration criteria (CCC/SPCC) have been met, each target is evaluated for linearity. Refer to SOP AN67: *Evaluation of Calibration Curves* for guidance.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where:

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds and their associated internal standard)
Cx = concentration of the target compound being measured (ug/mL)
Cis = concentration of the internal standard (ug/mL)

A linear or quadratic curve may be used to define the concentration/response relationship. If r^2 is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire concentration range.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of the tune/column evaluation solution (10.2.1.1). The tune and column evaluation criteria (10.2.1.3 and 10.2.1.4) must be met before the analysis of the calibration check standards can take place.

10.3.1 After the tune and column evaluation criteria have been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a mid-level concentration. The CCC and SPCC criteria (SOP Summary, Appendix A) must be met before the analysis of samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration (ug/mL)
Cccv = measured concentration using the selected quantitation method (ug/mL)

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If these criteria are not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.3.2 The continuing calibration verification standard (CCV) must also be evaluated for internal standard response.

If the extracted ion current profile (EICP) area for any of the internal standards in the CCV changes by more than a factor of two (-50% to +100%) from the last initial calibration sequence, the analytical system must be inspected for problems and corrective action instituted.

10.4 Samples are analyzed only after the DFTPP criteria, column evaluation criteria and the calibration verification criteria have been met. The analytical system must be evaluated every 12 hours by the analysis and evaluation of the tune/column evaluation standard and a mid-level calibration standard.

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- Minimum of five cal levels	Mid point calibration verification Optional RL: Standard-low point on cal curve
Samples analyzed until 12-hour clock expires	Samples analyzed until 12-hour clock expires

10.4.1 Remove the sample extracts to be analyzed from the refrigerator and allow the sample to come to ambient temperature.

10.4.2 Add 20-uL of the internal standard mix (2000 ug/mL) to each 1.0mL aliquot of the sample extract. The concentration of the internal standard in the extract is 40 g/mL.

10.4.3 Mix the contents of the autosampler vial by inverting several times.

10.4.4 Analyze the samples using the same analytical conditions used for the initial and continuing calibration standard. Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

10.4.5 The dilution factor is calculated by dividing the volume of sample extract in microliters into 1000. For example, if 100uL of a sample extract are diluted to final volume of 1.0mL, the dilution factor is 10. (1000/100 = 10). The following table gives some dilution factors:

Dilution Preparation

uL extract-Vext	uL MeCl2	volume of dilution (Vdil-uL)	uL ISTD (2000ug/mL)-Vistd	DF
1000	0	1000	20	1
500	500	1000	10*	2
200	800	1000	16*	5
100	900	1000	18*	10
50	950	1000	19*	20
20	980	1000	20*	50

*assumes dilution of a 1mL extract or 1mL aliquot of an extract that has been spiked with the internal standard at 40ug/mL using 20ul of a 2000ug/mL internal standard solution

The concentration of internal standards must remain constant for all extracts and extract dilutions at 40ug/mL. The following equation can be used to determine the volume of the 2000ug/mL internal standard solution to add to an extract when a dilution is prepared from an extract that has already been spiked with the internal standard solution:

$$Vistd(uL) = 20uL - \left(\frac{Vext}{Vdil} \otimes 20ul\right)$$

Vistd = volume of 2000ug/mL internal standard to add to the diluted extract (uL)
Vext = volume of extract used to prepare the dilution (uL)
Vdil = final volume of the dilution (uL)-1000uL (1.0mL)

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis

11.1.1 Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from the daily calibration standard or a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1.1 Two criteria must be met in order to positively identify a compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\text{retention time of the target compound}}{\text{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. Ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.1.2 Tentatively Identified Compounds (TICs)

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification.

The default procedure is to evaluate up to 20 compounds of greatest apparent concentration that are not included as target compounds or routinely reported volatile compounds. The unknown compounds are tentatively identified using a forward search of the reference library.

If the library search produces a match at or above 85%, report that compound. If the library search produces more than one compound at or above 85%, report the first compound (the highest match quality). If the library search produces no matches at or above 85%, report the compound as unknown. If possible, provide a general classification of the unknown – for example, unknown aromatic, unknown hydrocarbon, etc.

TICs should be evaluated within the retention time range from the first eluting target or surrogate (whichever is first in the target list) to three minutes after the elution of the last target compound.

11.1.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.1.2.2 The relative intensities of the major ions should agree within +/-20%.

11.1.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.1.2.4 Ions present in the sample spectrum, but not in the reference spectrum, should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.1.2.5 Ions present in the reference spectrum, but not in the sample spectrum, should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.1.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult senior analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.1.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculations assume that the same volume is injected for standards and samples.

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{V} \otimes DF$$

where:

Cis =	concentration of the internal standard (ug/mL)
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract (mL)
V =	volume of sample extract (L)
DF =	dilution factor

Soils

$$TIC\ (ug/kg, dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{F}{(W)(solids)} \otimes DF$$

where:

Cis =	concentration of the internal standard, ug/mL
AREAis =	total ion peak area of the internal standard
AREAtic=	total ion peak area of the TIC
F =	final volume of extract mL
W =	weight of sample analyzed (kg)
solids =	decimal equivalent of percent solids

11.2 Calculations for Samples-Internal Standard Technique
These calculations assume that the same volume is injected for standards and samples and that the standards and samples have the same concentration of internal standard.

11.2.1 Aqueous Samples

11.2.1.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{V} \otimes DF$$

where:

Ax =	area of the characteristic ion of the compound being measured
Ais =	area of the characteristic ion of the internal standard
Cis =	concentration of the internal standard (ug/mL)
RRFavg =	average response factor of the compound being measured
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.2 If a regression curve is used, the concentration is given:

$$concentration(ug/L) = Ccurve \otimes \frac{F}{V} \otimes DF$$

where:

C_{curve} =	concentration from curve (ug/mL)
F =	final volume of extract (mL)
V =	volume of sample extracted (L)
DF =	dilution factor

11.2.1.3 The reporting limit (RL) for each sample is given:

$$RL(ug/L) = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Vqap}{V} \otimes DF$$

where:

F = final volume of extract (mL)
Fqap = 1.0mL
Vqap = 1.0L
V = volume of sample extracted
DF = dilution factor. The LQM RL assumes a DF of 1.

NOTE: If V = 800mL to 1200mL, assume that Vqap/ V = 1 in the calculation of the reporting limit.

11.2.2 Soils

11.2.2.1 If the relative response factor is used, the calculation for samples is :

$$concentration(ug/kg, dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/mL)
RRFavg = average response factor of the compound being measured
F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100
DF = dilution factor

11.2.2.2 If the regression curve is used, the concentration is given:

$$conc(ug/kg, dw) = Ccurve \otimes \frac{F}{(W)(solids)} \otimes DF$$

where

Ccurve = concentration from curve(ug/mL)
W = weight of sample extracted (kg)
F = final volume of extract (mL)
solids = (percent solids)/100)
DF = dilution factor

11.2.2.3 The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{F}{Fqap} \otimes \frac{Wqap}{(W)(solids)} \otimes DF$$

where
F = final volume of extract (mL)
W = weight of sample extracted (kg)
solids = (percent solids)/100

The LQM assumes Wqap = 30g, solids = 1, Fqap = 1.0mL, and DF = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in AN02: *Analytical Batching.* SOP AN02 also describes the procedure for evaluating batch-specific QC. The QA/QC criteria are summarized in the SOP Summary (Appendix A).

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must participate in the analysis of samples by this procedure in accordance with SOP CA92: *Evaluation of IDOCs.*

12.3 Method Detection Limit

The method detection limit is determined in accordance with SOP CA90: *Procedure for the Determination of the Method Detection Limit.*

13.0 PREVENTIVE MAINTENANCE & TROUBLESHOOTING

Refer to SOP AN53: *Preventive Maintenance Procedures for Laboratory Instruments* for guidance.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Refer to SOP CA70: *Waste Management* for proper waste handling procedures.

15.0 REFERENCES

15.1 *STL Savannah Laboratory Quality Manual* current revision.

15.2 Method 8270C: *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846;* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

APPENDIX A
8270C SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	none; 4C	1-L amber	7 days	40 days
Soil/ Sediment	none; 4C	500-mL	14 days	40 days
Waste	none; 4C	Glass	14 days	40 days
TCLP	none; 4C	1-L amber	7 days	40 days

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
Tune/Column Evaluation Standard Clock starts at injection	Tune/Column Evaluation Standard Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification standard RL Standard (lowest point on calibration curve if required by client or state-specific QAP)
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

SEMIVOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION (DFTPP)	
m/e	**Ion Abundance Criteria (1)**
51	30-80% of mass 442
68	Less than 2.0% of mass 69
69	Present
70	Less than 2.0% of mass 69
127	25-75% of mass 198
197	Less than 1% of mass 198
198	Base peak, 100% relative abundance
199	5.0-9.0% of mass 198
275	10-30% of mass 198
365	Greater than 0.75% of mass 198
441	Present but less than mass 443
442	40-110% of mass 198
443	15.0-24.0% of mass 442

(1) 8270 criteria taken from CLP OLMO4.0 (January 1998). The use of alternate criteria is expressly allowed in SW-846 Method 8270C.

APPENDIX A
8270C SOP SUMMARY

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Phenol, 1,4-Dichlorobenzene, 2-Nitrophenol, 2,4-Dichlorophenol, Hexachlorobutadiene, 4-Chloro-3-methylphenol, 2,4,6-Trichlorophenol, Acenapthene, N-Nitrosodiphenylamine, Pentachlorophenol, Fluoranthene, Di-n-octylphthalate, Benzo(a) pyrene

System Performance Check Compounds-SPCC
N-Nitrosodi-n-propylamine, Hexachlorocyclopentadiene, 2,4-Dinitrophenol, 4-Nitrophenol

Initial Calibration	Continuing Calibration*
CCC: <= 30% RSD SPCC: RRFavg >= 0.050	CCC: <= 20% difference from initial calibration SPCC: RRF>= 0.050

*If CCC and/or SPCC do not meet the stated criteria, all targets that are reported must meet the CCC criteria.

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

The results for all target compounds are evaluated for linearity. If the %RSD is less than 15%, the calibration is assumed linear through the origin and the average response factor can be used for quantitation. If the average response factor for the target exceeds 15% (including any CCC), the analyst must use the calibration curve option.

NOTE: The lab has the option of using a regression curve for all analytes.

A linear, quadratic, or higher order regression fit may be used to define the concentration/response relationship. If r^2 is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range. The minimum number of calibration standards required for a regression curve are given in the following table:

Type of curve	Minimum Number of Calibration Points
Linear (first order)	5
Quadratic (second order)	6

QC Item	Frequency	Acceptance Criteria	Corrective Action
Tune/Column Evaluation Standard DFTPP 50ng Pentachlorophenol - 50ng Benzidine – 50ng p,p'-DDT 50ng	Prior to analysis of calibration standards every 12 hours	DFTPP - within criteria	-Evaluate alternative scans -Reanalyze and evaluate -Retune and reanalyze -Clean source, retune, reanalyze
		Pentachlorophenol and benzidine - present at usual response with no peak tailing visible p,p'-DDT - %breakdown <20%	-Reanalyze -Perform injector port maintenance and reanalyze -Cut more than usual length of column and reanalyze -Replace column
Initial Calibration	After Tune Check and when calibration verification standard fails acceptance criteria. All initial calibration standards	CCC: %RSD < 30% SPCC: RRFavg > 0.050 Use regression curve for quantitation if %RSD for any target compound exceeds 15%	-Reanalyze standard(s) -Prepare new standard(s) and reanalyze -Perform injector port maintenance and reanalyze standards -Retune and reanalyze standards -Replace column and reanalyze standards -Clean source and reanalyze standards
Continuing Calibration Verification	After tune check; every 12 hours prior to analysis of samples	CCC: %Difference <= 20% Or %Drift <= 20% SPCC: RRF >= 0.050	-Reanalyze standard -Prepare new standard and reanalyze -Recalibrate
Internal Standard Areas	Evaluate all standards and samples	Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence Areas in samples should be evaluated for gross error. Consult supervisor Retention time of internal standard must be +/-30 seconds from internal standard in previous CCV.	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Perform instrument maintenance and reanalyze extract -Re-extract and reanalyze if sufficient sample available -Recalibrate

QC Item	Frequency	Acceptance Criteria	Corrective Action
Surrogate recovery	Evaluate for all samples and QC items if extract is not diluted OR If diluted, where >RL	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract(s) -Re-extract and reanalyze if sufficient sample available
Method Blank	Per batch	All targets < RL in LQM	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
Lab Control Standard (LCS) - QAP subset	Per batch See SOP AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
Matrix spike (MS) Matrix spike duplicate (MSD)	Per batch if sufficient sample volume/weight supplied See SOP AN02	Within LQM Control Limits	-Evaluate chromatogram, spectra, and integrations -Reanalyze extract -Follow guidance in STL-SL SOP AN02
RL Standard (reporting limit)	Daily (optional)-lowest point on calibration curve if required by client or state-specific QAP	Detected at reasonable sensitivity	-Evaluate integrations and spectra; -Reanalyze -Prepare new standard and reanalyze
Initial Demonstration of Capability (IDOC)	Each work group	Accuracy and precision within method specified criteria	-Evaluate data -Reanalyze extracts if warranted -Re-extract and reanalyze for targets that fail criteria
Method Detection Limit (MDL)	Annually for each routine matrix See SOP CA90	Evaluate according to SOP CA90	Evaluate according to SOP CA90

APPENDIX B- TARGET COMPOUNDS

ROUTINE TARGET LIST

PARAMETER	RT	Quant Ion	Secondary Ions		ISTD
1,4-Dioxane	1.894	88	58	45	1
Pyridine	2.123	79	52	51	1
N-Nitrosodimethylamine	2.102	42	74		1
Aniline	3.812	93	66		1
Phenol	3.796	94	66	65	1
Bis(2-chloroethyl)ether	3.854	63	93	95	1
2-Chlorophenol	3.908	128	130	64	1
1,3-Dichlorobenzene	4.025	146	148	111	1
1,4-Dichlorobenzene	4.073	146	148	111	1
Benzyl Alcohol	4.202	108	79	77	1
1,2-Dichlorobenzene	4.239	146	148		1
2-Methylphenol	4.314	107	108	77	1
bis(2-Chloroisopropyl)ether	4.335	45	121		1
N-Nitroso-di-n-propylamine	4.469	70	42	101	1
3&4-Methylphenol	4.447	107	108		1
Hexachloroethane	4.522	117	201	199	1
Nitrobenzene	4.602	77	123	65	2
Isophorone	4.837	82	95	138	2
2-Nitrophenol	4.923	139	109	65	2
2,4-Dimethylphenol	4.965	107	122	121	2
Bis(2-chloroethoxy)methane	5.067	93	123	95	2
Benzoic acid	5.115	105	122		2
2,4-Dichlorophenol	5.169	162	164	98	2
1,2,4-Trichlorobenzene	5.259	180	182	145	2
Naphthalene	5.323	128	129		2
4-Chloroaniline	5.409	127	129	65	2
Hexachlorobutadiene	5.532	225	223	227	2
4-Chloro-3-methylphenol	5.991	107	144	142	2
2-Methylnaphthalene	6.135	142	141		2
1-Methylnaphthalene	6.269	142	141		2
Hexachlorocyclopentadiene	6.429	237	235	272	3
2,4,6-Trichlorophenol	6.541	196	198	200	3
2,4,5-Trichlorophenol	6.590	196	198	200	3
2-Chloronaphthalene	6.760	162	164	127	3
2-Nitroaniline	6.958	65	92	138	3
Dimethylphthalate	7.268	163	194	164	3
2,6-Dinitrotoluene	7.353	165	89	63	3
Acenaphthylene	7.337	152	151	153	3
3-Nitroaniline	7.540	138	108	92	3
Acenaphthene	7.599	154	153	152	3
2,4-Dinitrophenol	7.685	184	63	154	3
4-Nitrophenol	7.824	65	109	139	3
Dibenzofuran	7.829	168	139		3
2,4-Dinitrotoluene	7.914	165	89	63	3
2,3,4,5-Tetrachlorophenol	8.064	232	230	131	3
2,3,4,6-Tetrachlorophenol	8.091	232	230	131	3
Diethylphthalate	8.310	149	177	150	3

Fluorene	8.336	166	165	167	3
4-Chlorophenyl-phenylether	8.363	204	141	206	3
4-Nitroaniline	8.454	138	108	92	3
4,6-Dinitro-2-methylphenol	8.513	198	105	121	4
N-Nitrosodiphenylamine	8.555	169	168	167	4
1,2-Diphenylhydrazine	8.593	77	105	182	4
4-Bromophenyl-phenylether	9.090	248	250	141	4
Hexachlorobenzene	9.293	284	142	249	4
Pentachlorophenol	9.581	266	264	268	4
Phenanthrene	9.784	178	176	179	4
Anthracene	9.854	178	176	179	4
Carbazole	10.137	167			4
Di-n-Butylphthalate	10.847	149	150	104	4
Fluoranthene	11.659	202	203	101	4
Benzidine	11.926	184	92	185	5
Pyrene	12.006	202	200	203	5
Butylbenzylphthalate	13.214	149	91	206	5
3,3'-Dichlorobenzidine	13.892	252	254	126	5
Benzo(a)Anthracene	13.866	228	229	226	5
Bis(2-ethylhexyl)phthalate	14.111	149	167	279	5
Chrysene	13.924	228	226	229	5
Di-n-octylphthalate	14.971	149	43		5
Benzo(b)fluoranthene	15.367	252	253	125	6
Benzo(k)fluoranthene	15.399	252	253	125	6
Benzo(a)pyrene	15.783	252	125	253	6
Indeno(1,2,3-cd)pyrene	17.284	276	139		6
Dibenzo(a,h)anthracene	17.317	278	139	279	6
Benzo(g,h,i)perylene	17.674	276	277	138	6
SURROGATES					
2-Fluorophenol	3.032	112	64		1
Phenol-d5	3.785	99	71		1
Nitrobenzene-d5	4.586	82	128	54	2
2-Fluorobiphenyl	6.643	172	171		3
2,4,6-Tribromophenol	8.732	330	332	141	3
Terphenyl-d14	12.332	244	122	212	5
INTERNAL STANDARDS					
1,4-Dichlorobenzene-d4	4.057	152	150	115	1
Naphthalene-d8	5.302	136	68		2
Acenaphthene-d10	7.556	164	162	160	3
Phenanthrene-d10	9.747	188	94	80	4
Chrysene-d12	13.887	240	236	120	5
Perylene-d12	15.858	264	265	260	6

APPENDIX B- TARGET COMPOUNDS

APPENDIX IX TARGET LIST

PARAMETER	RT	Quant Ion	Secondary Ions			ISTD
1,4-Dioxane	1.933	88	58	45		1
Pyridine	2.178	79	52	51		1
2-Picoline	2.664	93	66			1
1,4-Benzoquinone	4.466	54	108	82		1
N-Nitrosomethylethylamine	2.739	88	42	43	56	1
Methyl methanesulfonate	2.964	80	79	65		1
N-Nitrosodiethylamine	3.268	102	42	44	57	1
Ethyl methanesulfonate	*3.503*	*79*	*109*	*97*	*45*	*1*
N-Nitrosopyrrolidine	4.481	100	41	42		2
Acetophenone	4.486	105	77	51		2
N-Nitrosomorpholine	4.497	56	86			1
O-Toluidine	4.529	106	107	79		2
Phorate	9.123	75	121			4
N-Nitrosopiperidine	4.796	114	42	55	56	2
O,O,O-Triethyphosphorothioate	5.122	65	97	93		2
2,6-Dichlorophenol	5.469	162	164	98		2
Hexachloropropene	5.507	213	211	215	117	2
[illegible]4,5-Tetrachlorobenzene	6.447	216	214	179		3
[illegible]Dimethylphenethylamine	5.619	58	91	42		2
[illegible]Nitroso-di-n-butylamine	5.875	84	57	41		2
1,4-Phenylenediamine	5.864	108	80	107		2
Safrole	6.094	162	104	135	103	2
Isosafrole	6.757	162	104	131		2
1,1-Biphenyl	6.805	154	76			3
1,4-Naphthoquinone	7.056	158	104	76		3
m-Dinitrobenzene	7.317	168	76	50		3
Pentachlorobenzene	7.916	250	248	252	215	3
1-Naphthylamine	8.001	143	115	116		3
2-Naphthylamine	8.113	143	115	116		3
2,3,4,6-Tetrachlorophenol	8.140	232	230			3
5-Nitro-o-toluidine	8.466	152	77	106		3
Thionazin	8.471	107	96	97		4
Sulfotepp	9.032	97	65			4
1,3,5-Trinitrobenzene	9.091	213	74	120		4
1-Diallate	9.118	86	43	234		4
Phenacetin	9.161	108	109	179		3
2-Diallate	9.235	86	43	234		4
Dimethoate	9.396	87	93	125		4
4-Aminobiphenyl	9.556	169	168	170		4
Pronamide	9.748	173	175	145		4
Pentachloronitrobenzene	9.748	237	295	142	214	4
[illegible]ulfoton	9.935	88	60			4
[illegible]oseb	9.957	211	163	147		4
[illegible]ethyl parathion	10.517	109	125			4
4-Nitroquinoline-1-oxide	11.094	174	101	128	75	4
Parathion	11.158	109	97			4
Famphur	13.178	218	93	125		4

Methapyrilene	11.388	97	58	191		4
Aramite-1	12.435	185	191	319		5
Aramite-2	12.563	185	191	319		5
p-Dimethylaminoazobenzene	12.638	120	225	77		5
Chlorbenzilate	12.745	139	251	75		4
Kepone	**17.739**	272	270	237		5
3,3'-Dimethylbenzidine	13.167	212	196	106		5
2-Acetylaminofluorene	13.562	181	180	223		5
7,12-Dimethylbenz(a)anthracene	15.438	256	239	241		6
Hexachlorophene	15.747	196	198			6
3-Methylcholanthrene	16.324	268	252	253		6
INTERNAL STANDARDS						
1,4-Dichlorobenzene-d4	4.102	152	150	115		1
Naphthalene-d8	5.346	136	68			2
Acenaphthene-d10	7.601	164	162	160		3
Phenanthrene-d10	9.802	188	94	189		4
Chrysene-d12	13.926	240	236	120		5
Perylene-d12	15.902	264	265	260		6

FIGURE 1 – Tailing Factor Calculation

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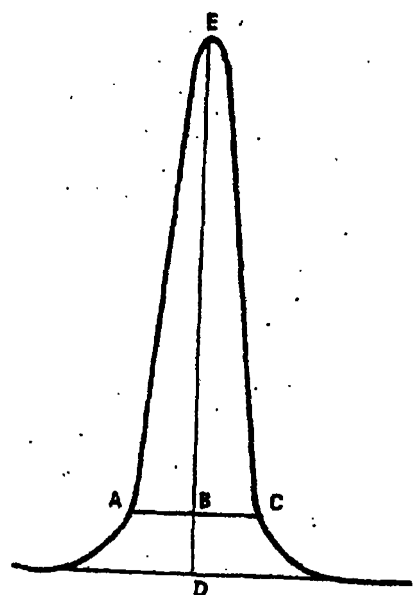

TAILING FACTOR= $\frac{BC}{AB}$

Example calculation: Peak Height = DE = 100 mm
10% Peak Height = BD = 10 mm
Peak Width at 10% Peak Height = AC = 23 mm
AB = 11 mm
BC = 12 mm

Therefore: Tailing Factor = $\frac{12}{11}$ = 1.1

SEVERN TRENT SERVICES

VOLATILE ORGANIC COMPOUNDS IN WATER, SOIL, AND WASTE BY GAS CHROMATOGRAPHY (SW-846 8021 AND 8015)

Approved by:

R. Wayne Robb — 9 Jan 2002

Signature — Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This procedure can be used to identify and quantify volatile organic compounds (VOC) in aqueous samples, soils and sediments, and waste samples by purge and trap/gas chromatography. Table 1 lists the routine target compounds and an example of the retention time order of the routine target compounds. If an extended list of compounds is required beyond those listed in Table 1, 8260B will be employed because many peaks in the extended list cannot be chromatographically resolved.

1.2 The reporting limit(RL), the method detection limit(MDL), and the accuracy and precision limits are listed in the current revision of the Laboratory Quality Manual prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINTIONS

2.1 Volatile organic compounds (VOC) are purged from the sample matrix with helium, swept onto a sorbent material where the VOC are trapped, and thermally desorbed onto a GC column. The GC is temperature-programmed to separate the VOC which are then detected by a Hall electrolytic conductivity detector (HECD) in series with a photoionization detector (PID) or connected via a sampler splitter to a PID or flame ionization detector (FID). The FID is used when 8015B compounds are to be reported. Qualitative identification of the target compounds in the sample is based on the retention time. Quantitative analysis is performed using the internal standard technique.

2.2 Aqueous samples may be purged at ambient conditions (recommended) or at 40C (optional). Five to twenty-five milliliter aliquots of the sample may be purged. The calibration standards and the associated QC must be analyzed under the same conditions and volume.

2.3 Low level (<1mg/kg) soil samples are purged at 40C in a purge and trap instrument designed to meet the requirements of SW-846 Method 5035. The sample is stirred during purging to thoroughly mix the soil and water. The calibration standards are purged under the same conditions. The minimum weight of sample that can be used for direct purging is 1g.

NOTE: Many agencies and clients are requiring the use of SW-846 5030 for soils. SL will support these requests but will use 5035 as the default procedure for the purge and trap analysis of low level soils.

2.4 High level soils(>1mg/kg) and waste samples are extracted with methanol. A portion of the methanol extract is injected into reagent water. The methanol extract/reagent water is purged at ambient temperature using the same instrument conditions and calibration used for aqueous samples.

2.5 This procedure is based on the guidance in SW-846 Methods 8021B, 8015B, and 8000B. In some instances, volatile petroleum products (e.g., GRO) can be determined concurrently with the VOC target compounds.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 The analyst should wear a lab coat or apron, eye protection (lab glasses or face shield) and gloves when preparing standards and handling samples. Samples and standards should be handled under a hood or in a well-ventilated area.

3.3 The analyst should be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in the lab. The MSDS list the potential hazards that each material poses and information about safe handling of the material.

4.0 INTERFERNCES

4.1 Contamination may occur from diffusion of VOCs into the sample during shipping and storage. Fluorocarbons and methylene chloride may penetrate the Teflon septa of the sample vial. Sampling and storage areas should be as free from volatile contamination as possible. Trip blanks should be prepared and analyzed to check for this type of contamination.

4.2 Care must be taken to ensure that the analysis area is also free of aerosols and vapors. Contaminants in the air can diffuse into samples during preparation and loading. Many spray cleaners, typewriter cleaners, paints, varnishes, and furniture and carpet cleaners have solvents that may affect the VOC analysis.

4.3 Contamination by carryover can occur when high level and low level samples are run sequentially. Cross contamination can also occur from syringes and purge tubes that are not properly cleaned and rinsed. Purge tubes should be cleaned with hot, soapy water, rinsed with tap water, and then dried at 105°C until dry. Syringes should be cleaned by rinsing repeatedly with methanol and reagent water.

4.4 Some care should be taken in the maintenance of the Teflon ferrules and seals used on the purge and trap concentrators. These Teflon fittings are routinely checked and replaced as needed. Purge and trap lines can also become contaminated and can be cleaned using the procedure supplied by Tekmar.

4.5 The addition of acid to liquid samples prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The addition of acid will cause the breakdown of 2-chloroethyl vinyl ether.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquid samples are collected with no headspace in 40mL vials fitted with Teflon-lined caps. The samples are acidified at the time of collection with HCl . The sample must be iced at the time of collection and stored at 4C (less than 6C with no frozen samples) until analysis. The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for unpreserved samples is 7 days.

If the sample pH is greater than 2, acid may be added through the septum to bring the pH <2. A "sacrificial" vial or a vial used for screening analysis is used to check the sample pH and to determine the amount of acid required to bring the pH below 2. Do not add more than 400uL (0.40mL) of 1:1 HCl to a VOC vial. If pH cannot be adjusted to <=2 without destroying the integrity of the sample, the sample must be analyzed within 7 days of collection.

5.2 Soils: Soils are routinely collected in duplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with Teflon-lined caps. The bulk sample may be used for direct purging by SW-846 5030 or the methanol extraction if the concentration of the direct purge exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be transferred within 48 hours to a sealed vial containing sodium bisulfate solution or frozen in water to preserve the sample. The hold time of the preserved sample is 14 days from the date of collection. The procedure for preparing soil samples is given in Section 9.2.

5.3 Waste samples are collected in glass containers (usually 40mL clear glass) equipped with Teflon-lined caps. The holding time for waste samples is 14 days from date of collection. The procedure for the preparation of wastes is given in section 9.3.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See SL-SOP AN70. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph (GC)-temperature programmable equipped with a Hall Electrolytic Conductivity Detector (HECD) and either a flame ionization detector(FID) or photoionization detector(PID).

6.2 Purge and trap(P/T) system compatible with the GC, consisting of a concentrator and compatible autosampler.

6.3 Archon Soil Analyzer

6.4 Data system or integrator compatible with the GC and P/T device

6.5 P/T Trap: VOCARB 3000 or "three ring trap" consisting of charcoal, silica gel, and Tenax

6.6 Recommended Columns and Column configuration for aromatics and halogenated compounds-

DB-VRX fused silica capillary column, 60M X 0.45 mm i.d., 2.5 mm film
DB-624 fused silica capillary column, 75M X 0.53 mm i.d., 3.0 mm film
Restek 502.2 fused silica capillary column, 60M X 0.53 mm i.d., 3.0 mm film

The recommended configuration is connecting two columns of the same length and type to the transfer line of the P/T or injector port with a glass y-splitter. One column is connected to the HECD and the other column to the FID or PID. This configuration allows higher desorb flows because the sample is split between two columns. The result is better chromatography and an extended working range with little or no loss in sensitivity. The GC may also be configured with a single column connected to a PID in series with an HECD. If only BTEX other non-halogenated targets are requested, the instrument configuration in SL SOP VG15 may be used (PID/FID).

6.7 Syringes, gastight: appropriate volumes

6.8 Solution storage container with Teflon-lined screw caps, 15-mL

6.9 Analytical balance, capable of accurately weighing +/-0.0001 gram

6.10 Top loading balance, capable of accurately weighing +/-0.01 gram

7.0 REAGENTS

Reagents must be tracked in accordance with SL SOP AN44:*Reagent Traceability.*

7.1 Methanol: Burdick and Jackson Purge and Trap Grade Methanol

7.2 Reagent water: Deionized or deep well water. The water may require purging prior to use to eliminate VOCs: Fill up the purge vessel with reagent water and purge with nitrogen for at least four hours before use. Check water for background prior to general lab use as reagent water. Maintain constant purge through water and vessel.

7.3 Sodium bisulfate-reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Soil preservation solution- Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC-especially water soluble solvents such as acetone.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with SL SOP AN41: *Standard Material Traceability.*

8.1 Preparation of Calibration Standards

8.1.1 Preparation of **Stock Standards** from Neat Compounds

The lab should attempt to obtain a certified primary standard or secondary standard before preparing stock standards from neat materials. If primary stock standards must be prepared in-house, the target concentration range is from 2000ug/mL to 10000ug/mL. SL-SOP AN43: *Standard Preparation* gives the general instructions for the preparation of the stock solutions from neat materials.

8.1.2 Preparation of the **Working Standard** from Stock Standards

The working standard is prepared from the primary stock standards that are either prepared from neat compounds or purchased as certified solutions. The working standard contains one or more of the target compounds at a concentration suitable for preparing the calibration standards, generally 10-200ug/mL. A known volume of the working standard is then added to a known volume of reagent water to make the calibration standard.

The standards and standard concentrations listed in Table 2 are the suggested for routine use. If other "recipes" are used, the lab must document the standard preparation procedures in the standard traceability log.

8.1.3 Preparation of the **Calibration Standards** from the Working Standards

The calibration standard is made by adding a known volume of the working standard to a known volume of reagent water. The instrument must be calibrated using a minimum of five calibration standards. The lowest level standard must be at the reporting limit and the rest of the standards will define the working range of the analytical system.

The calibration standards listed in Table 3 are suggested for routine use. If other "recipes" are used, the lab must document these standard preparation procedures in the standard traceability log.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance provided in SL-SOP AN71: *Compositing of Samples.*

9.1 Liquid samples are analyzed directly by purge and trap/GC-MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded at the time of analysis to determine if the sample has been properly preserved.

9.2 Preparation of Soil Samples

9.2.1 Remove the Encore samples and the bulk sample from the storage area.

9.2.2 Test an aliquot of the bulk sample for the presence of carbonates.

- Transfer 5g of sample from the bulk sample to a 40mL vial..
- Add 5ml of the sodium bisulfate solution and shake the vial .
- If the sample exhibits effervescence, the Encore samples should be preserved as described above using 5mL of volatile-free water in place of the sodium bisulfate solution and placed in a freezer at –10C. The analytical hold time for frozen samples is 14 days from collection.
- If no effervescence is noted, the Encore samples may be preserved with 5mL soil preservation solution.

9.2.3 Add a stir bar to a vial and weigh the vial and record its tare weight(or tare the vial and stir bar weight by pressing the autotare button).

9.2.4 Transfer the sample from the Encore sampler to the tared vial and record the weight of the sample.

If the sample effervesced during the carbonate test (9.2.2), add 5.0mL of reagent water and freeze at –10C. The hold time is 14 days from collection

If not, add 5.0mL of the soil preservation solution, seal the vial, and store the sample at 4C until the time of analysis. The preserved sample must be analyzed within 14 days of collection.

NOTE: A preparation blank is prepared when Encore samples are transferred. The preparation blank contains the same reagents as the samples-either 5mL of reagent water or 5mL of soil preservation solution.

9.3 A methanol extraction is prepared if the concentration of the sample purged directly exceeds the working range of the system. The bulk sample, collected in the 125-mL sample container, or an extra Encore(if available) may be used to prepare the methanol extraction. Carry out the preparation quickly to minimize the loss of volatiles.

The following example extraction procedure is designed to result in the same on-column amounts of the surrogates as in the ambient water purge; that is, in this example, BCM will be at 250ng and a,a,a-TFT will be at 750ng on column when 125uL of the extract is analyzed. Note that the surrogates can be diluted out if a large dilution is required.

-Mix the sample with a stainless steel spatula and transfer 10g (+/- 0.5g) to a glass vial.

-Add 20uL of the 1000ug/mL BCM stock and 30uL of the 2000ug/mL a,a,a-TFT stock to the sample and quickly add 10mL of purge and trap grade methanol. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 10g and 100% percent solids, is calculated:

$$BCM(ug/kg,dw) = \frac{20uL \otimes 1000ug/mL}{10g \otimes solids} \otimes \frac{0.020mL \otimes 1000ug/mL}{0.010kg \otimes solids} = 2000ug/kg,dw$$

$$a,a,a-TFT(ug/kg,dw) = \frac{30uL \otimes 2000ug/mL}{10g \otimes solids} \otimes \frac{0.030mL \otimes 2000ug/mL}{0.010kg \otimes solids} = 6000ug/kg,dw$$

-Shake the sample for one minute. Allow the solvent to separate from the solids portion of the sample and transfer a 1-2mL aliquot of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

-For each batch of twenty or fewer samples, prepare a method blank and a lab control standard.

The method blank is prepared by adding 20uL of the BCM stock and 30uL of the a,a,a-TFT stock to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The lab control standard is prepared by adding 20uL of the BCM stock, 30uL of the a,a,a-TFT stock, and 4uL of the 2500ug/mL matrix spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

NOTE: If requested, prepare the MS/MSD in the same manner as the LCS, substituting client sample for blank sand or soil.

-Add 125uL of the extract (or a smaller volume) to 25.0mL of water (or to 5.0mL if the calibration is based on 5.0mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

9.4 Methanol Extraction for Wastes

The following extraction procedure is designed to result in the same on-column amounts of the surrogates as in the ambient water purge; that is , BCM will be at 250ng and a,a,a-TFT will be at 750ng on column when 125uL of the extract is analyzed. Note that the surrogates can be diluted out is a large dilution is required.

Carry out the preparation quickly to minimize the loss of volatiles.

-Mix the sample with a stainless steel spatula and transfer 1g (+/- 0.2g) to a glass vial.

-Add 20uL of the BCM stock (1000ug/mL) and 30uL of the a,a,a-TFT stock (2000ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. If the sample is completely soluble in the methanol, dilute to a final volume of 10mL The theoretical concentration of the surrogates in the sample, assuming a sample weight of 1.0g , is calculated:

$$BCM(ug/kg) = \frac{0.020mL \otimes 1000ug/mL}{0.0010g \otimes solids} = 20000ug/kg$$

$$a,a,a - TFT(ug/kg) = \frac{0.030mL \otimes 2000ug/mL}{0.0010g \otimes solids} = 60000ug/kg$$

-Shake the sample for one minute. Allow the solvent to separate from the solids portion of the sample and transfer a 1-2mL aliquot of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

-For each batch of twenty or fewer samples, prepare a method blank and lab spike.

-The method blank is prepared by adding 10uL of the BCM stock (2000ug/mL) and 30uL of the a,a,a-TFT stock (2000ug/mL) to 10mL of purge and trap grade methanol. Assume a sample weight of 1.0g. Analyze 125uL of the extract.

-The lab control standard is prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 8uL of the matrix spiking solution (2500ug/mL) to 5.0mL of purge and trap grade methanol. Assume a sample weight of 5.0g. Analyze 125uL of the extract.

-Add 125uL of the extract (or a smaller volume) to 25.0mL of water (or to 5.0mL if the calibration is based on 5.0mL). Add 5uL of the internal standard solution and analyze the sample using the ambient water calibration.

NOTE: Waste samples will usually require significant dilution prior to analysis.

10.0 ANALYTICAL PROCEDURE

10.1 Instrument Conditions

The conditions listed in this section are for general guidance. The lab should optimize the analytical system conditions to maximize separation and sensitivity while minimizing run time. The conditions used by the lab must be documented in the instrument maintenance log, on the sample run log, or in the data system. The recommended instrument conditions for the analysis of BTEX are given in SL SOP VG15.

GC Conditions/Temperature Program-EXAMPLE

Initial Temperature	40C for 10 minutes
Temperature program	8C per minute
Final Temperature	220C –hold until last target elutes and add 2-3 minutes (~30-35 minutes total run time)
Column flow	8-10ml/min helium through each column
Injector Temperature	200C
Detector Temperature	300C

P/T Conditions-VOCARB 3000 trap-EXAMPLE

Purge time	11 minutes
Purge Temperature	Aqueous-ambient; Soils 40C
Purge flow	Approximately 30ml/min(note 1).
Dry Purge	5 minutes
Desorb Temperature	250C
Desorb time	2-6 minutes
Bake Temperature	260C for 10 minutes
Valve and line temperatures	100-110C

P/T Conditions-three ring trap-charcoal, Tenax, silica gel-EXAMPLE

Purge time	11 minutes
Purge Temperature	Aqueous-ambient; soils-40C
Purge flow	Approximately 30ml/min(note1).
Desorb Temperature	180C
Dry Purge	5 minutes
Desorb time	2-4 minutes
Bake Temperature	225C for 10 minutes
Valve and line temperatures	100-110C

NOTE 1: Purge flow adjusted to balance the response of chloromethane and bromoform. The purge flow must be balanced for adequate sensitivity of the target compounds. If the purge flow is too high, the response of the gases will be low and not reproducible. If the purge flow is too low, the response of the more water soluble targets-ketones, ethers, bromoform-may be low and the reporting limit may not be achieved on a routine basis.

NOTE 2: A dry purge of 5 minutes is recommended to remove water from the trap prior to desorb. Water and excessive methanol elute in the same retention time range as the gases and may cause erratic response or some loss of response of these compounds. The use of the hydrophobic Carbotrap 3000 trap will also help to minimize water.

10.2 Initial Calibration

10.2.1 Prepare the initial calibration standards. The lab must document the "recipe" used to prepare the calibration standards. An example of a standard preparation is given in Section 8. For 600-series, the minimum number of calibration levels is three (3); for 8000-series, the minimum number of calibration points is five (5).

-Remove the plunger from the syringe and fill the barrel to overflowing with reagent water(syringe valve in the "red" position).

-Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL or 25mL)

-Briefly remove the syringe valve and inject the standards and internal standards into the syringe.

NOTE: Use the internal standard(IST) mix when preparing the calibration standards for analysis. The surrogates are already included in the standard mixes.

Alternatively, the calibration standards can be prepared in larger volumes by adding the working standards to reagent water contained in volumetric flasks. The volume of methanol introduced into the purge and trap and GC should be held to the lowest volume possible to reduce interferences due to methanol.

NOTE: The standards for Low level soil samples are prepared in the same manner as the water standards. The standards for the Low level soils are purged at 40C. The lab has the option of using blank sand or soil in the calibration standards and the method blank in the low level soil analysis.

10.2.2 Load the standard(s) onto the purge and trap device and begin the analysis. All pertinent information concerning the standards must be recorded on the analysis log. The standards must be clearly identified and traceable to the preparation steps.

10.2.3 After the acquisition has taken place, evaluate the calibration standards to ensure that each target compound, surrogate, and internal standard has been correctly identified. The analyst must be careful to complete this step before proceeding.

10.2.4 A calibration curve is established for each analyte by plotting the concentration along the x-axis and the corresponding response along the y-axis. A linear or quadratic regression fit may be used to define the concentration/response relationship. If the correlation coefficient of the linear regression curve is greater than 0.99, the curve can be used to quantify samples. The analyst must ensure that the regression curve accurately defines the concentration/response relationship over the entire calibration range.

Regression Type	Minimum number of Points	Acceptance Criterion
Linear	Five	Correlation >=0.99
Quadratic	Six	Coefficient of Determination >=0.99

10.2.5 Alternatively, the relative response factor for each target compound and surrogate can be calculated to evaluate the calibration curve using the data system. See Sop AN67:*Evalaution of Calibration Curves* for the equations used to calculate the relative response factor and relative standard deviation.

If the %RSD of the curve is less than or equal to 20%, the average RRF can be used for quantitation. If the %RSD exceeds 20%, the options are to 1) evaluate a linear or quadratic regression fit.(see SOP AN67); or 2) use the grand mean exception as described in SOP AN67.

NOTE: Use the hierarchy in SOP AN67 to determine the means to evaluate the curve. The use of the grand mean exception should be used only as a last resort and only for a short time because of the difficulty of tracking the

10.2.6 After the calibration criteria has been met, the method blank is analyzed. 5.0mL to 25mL of reagent water is spiked with the internal standard/surrogate and analyzed-the volume must be the same as the calibration standards. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the SL CQAP or other specified QAP.

If the method blank repeatedly fails to meet the criteria, contact the immediate supervisor to determine the cause of the problem and to determine a course of action. This action may include re-cleaning the sparging tubes (with soap, hot water, and methanol), purging the effected autosampler ports with heated methanol, flushing the purge and trap ALS concentrator with methanol, replacing the adsorbent trap, changing the transfer line, and changing the column. A method blank is then analyzed after taking the corrective action to demonstrate that the contamination has been eliminated. Once the system is determined to be free from contamination, sample analysis may begin. Method blanks may be required after the analysis of samples that contain very high levels of VOC.

10.3 Continuing Calibration Verification

10.3.1 The continuing calibration standard should be a concentration of 20ug/L for 5ml/25mL and 100ug/kg for a 5g sample. Prepare and analyze the CCV and compare the response to the initial calibration.

Calculate the percent drift or difference,

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration
Cc = measured concentration using the selected quantitation method

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

If the percent difference or percent drift is less than or equal to 15% for all target s except the gases and ketones, the calibration is verified and samples may be analyzed. The criterion for the gases and ketones is 20%. If the percent difference or percent drift is less than or equal to 20% for these compounds, the calibration curve is verified and samples may be analyzed.

Grand Mean Exception:

10.3.2 The calibration standard must also be evaluated for internal standard retention time and area.

If the retention time of any internal standard changes by more than 30 seconds from the last 12-hour calibration check, the analytical system must be inspected for problems and corrective action instituted.

If the area for any of the internal standards changes by more than a factor of two (-50% to +100%) from the last calibration check standard, the analytical system must be inspected for problems and corrective action instituted.

10.3.3 After the continuing calibration criteria has been met, the method blank is analyzed. And evalauted as in Section 10.2.6.

10.4 Sample Analysis- Aqueous Samples-5ml or 25mL sample

This method allows the use of either a 5mL sample volume or a 25ml sample volume. The analyst must use the same volume as was used for the calibration standards-if a 5mL sample is used, it must be quanted off of the 5mL calibration curve; if a 25ml sample is used, it must be quanted off of the 25mL calibration curve. Samples are analyzed only after the initial or continuing calibration criteria has been met, and the method blank criteria has been met. Example sequences for the 600- and 8000-series methods are given in the SOP Summary at the end of this SOP.

10.4.1 Remove the samples to be analyzed from the refrigerator and allow the samples to come to ambient temperature.

10.4.2 Put on a pair of gloves before transferring the sample from the vial to the syringe. The sample is most likely preserved with acid or may contain toxic or hazardous chemicals or biologically active components that may cause skin irritations. ***No exceptions to this step-gloves must be worn when handling samples.***

10.4.3 Mix the contents of the vial by inverting the vial several times. Check to see if there are air bubbles present in the sample. If air bubbles are present, use another vial if available. Make a note on the analysis log if the sample used contained bubbles and notify the supervisor and/or the project manager.

10.4.4 Remove the plunger from the glass syringe. Attach a syringe valve to the syringe Luer-tip to prevent sample from spilling out of the syringe when sample is added.

10.4.5 Open the vial of the well mixed sample and gently pour the sample into the syringe barrel. The sample should fill the barrel of the syringe and overflow to allow trapped air bubbles to escape.

10.4.6 Replace the plunger into the syringe barrel. Try not to let air bubbles get into the barrel. If air bubbles are present, turn the syringe up, open the syringe valve , and expel the air while adjusting the volume to 5.0mL or 25mL. If no air bubbles were trapped, adjust the syringe to volume.

10.4.7 Open the syringe valve and inject the internal standard/surrogate (ISSU) mix into the sample.

10.4.8 Transfer the sample from the syringe to the purge and trap device. Record all of the sample identification information on the analysis log. Check the pH of the sample with pH paper and record the pH on the instrument log or other appropriate log.

10.4.9 Analyze the samples using the purge and trap and GC conditions used for the initial and continuing calibration standards.

10.4.10 Determine the concentration of the samples and QC items. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

A dilution is made when a volume of the sample is mixed with the reagent water to a final volume of 25ml, depending on which curve is being used. The dilution reduces the concentration of the original sample to bring the concentration into the working range of the calibration curve.

The dilution factor is calculated by dividing the volume of sample into the volume used for the calibration curve.

$$DF = \frac{final\ volume\ of\ dilution(mL)}{volume\ of\ sample\ used(mL)}$$

For example, if 1.0mL of sample is diluted to final volume of 5.0mL, the dilution factor is 5. (5.0/1.0 = 5). If 1.0mL of sample is diluted to a final volume of 25mL, the dilution factor is 25 (25/1=25).

The following table gives some common dilution factors:

Volume of Sample (mL)	Volume of Reagent Water (mL)	Final Volume (mL)	Dilution factor
5.0	0	5.0	1
2.5	2.5	5.0	2
1.0	4.0	5.0	5
0.5	4.5	5.0	10
0.10	4.9	5.0	50
25.0	0	25.0	1
5.0	20.0	25.0	5
2.5	22.5	25.0	10
1.0	24.0	25.0	25
0.50	24.5	25.0	50
0.10	24.9	25.0	250

NOTE: The same volume of internal standard/surrogate mix (ISSU) is added to the dilution as was added to the undiluted sample.

10.5 Low Level Soil Samples by Heated Purge and Trap (Method 5035)

10.5.1 Remove the samples to be analyzed from the refrigerator (Section 9.2) and allow the samples to come to ambient temperature. Inspect the vial for cracks or obvious breaches in the septum.

10.5.2 Load the samples on to the Archon soil purging unit. Standards and QC items must be analyzed under the same heated purge and trap conditions. The general purge and trap conditions are given in Section 10.1.

10.5.3 Determine the concentration of the samples and QC items. If the concentration of a target compound is above the highest calibration standard, a smaller sample aliquot is weighed and analyzed. Do not use less than 1g of sample for the low level soils.

Sample Size	Nominal low range for concentration*	Nominal High range for concentration*
5.0g	5ug/kg	200ug/kg
1.0g	25ug/kg	1000ug/kg
MeOH extractions		
10g to 10mL- 0.125mL of extract	200ug/kg	8000ug/kg
1g to 10mL- 0.125mL of extract	2000ug/kg	80000ug/kg

* the nominal concentration is based on a 25ng on-column quantitation. Compounds with higher quantitation limits will be proportionally higher.

10.6 Analysis of Methanol Extracts of Soils/Solids

The methanol extraction is used when the concentration of one or more target compounds exceeds the linear range of the low level purge technique (>1000ug/kg). **Samples** are analyzed only after the 4-BFB criteria, the initial or continuing calibration criteria has been met, and the method blank criteria has been met. Medium level soil extracts are quanted using the ambient purge calibration curve. Sample preparation steps are included in Section 9.

Remove the plunger from the 5.0-mL syringe and fill the barrel to overflowing with reagent water(syringe valve in the "red" position).

Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL)

Briefly remove the syringe valve and inject the sample extract(maximum of 100uL) and 5uL of the internal standard (IST) solution into the syringe.

NOTE: Use the internal standard(IST) mix when preparing the medium level samples. Recall that the surrogates have already been added to the sample prior to methanol extraction.

Load the sample on to the purge and trap device and begin the analysis. All pertinent information concerning the samples must be recorded on the analysis log. The samples must be clearly identified and traceable to the extraction log. These conditions must be the same as was used for the initial and continuing calibration standards-ambient purge for aqueous samples.

Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, a smaller aliquot of the methanol extract is reanalyzed.

NOTE: *It is possible to dilute the surrogates in the sample extract below the linear range of the calibration curve.* The minimum extract aliquot that can be used to provide a quantifiable result for the surrogates and matrix spikes is 0.020mL (20uL). It is not probable that the recovery of the surrogates would be 100%, which is necessary to provide a quantifiable result using a 0.010mL(10uL) aliquot of the extract.

mL Methanol Extract	Surrogates- theoretical ng on-column (Hall)	Surrogates- theoretical ng on-column(PID or FID)
0.100	250	250
0.050	125	125
0.020	50	50
0.010	25-quantitation limit	25-quantitation limit
0.0050	12.5-below the quantitation limit	12.5-below the quantitation limit

10.8 Reporting Results from Dilutions

Unless otherwise specified by a client or QA plan, results from a single dilution are reportable as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range. When reporting results from dilutions, appropriate data flags should be used (*F34 or *F42) or qualification in a case narrative provided to the client. For TCLP analyses, every effort should be made to achieve the regulatory level without substantial instrument overload.

For clients who demand we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 the dilution factor with the highest target in the upper half of the calibration curve (i.e., a sample analyzed at a DF of 50 resulting in a hit in the upper half of the calibration curve would be reanalyzed at a DF of 5 to provide lower detection limits to the client). Project managers and lab staff must work together to balance client satisfaction with productivity.

11.0 DATA ANALYSIS/CALCULATIONS

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times), the recovery and retention time shift of the internal standards and surrogate compounds, and whether the peak response falls within the working range of the calibration. The qualitative determination of the presence of a compound will necessitate the calculation of the concentration of the suspected target compound; therefore, the integration of the peaks musts also be evaluated. Manual integrations must be documented in accordance with SL SOP AN65 and approved by a supervisor. The analyst must be thoroughly familiar with the calculations of Section 11.2. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data.

The qualitative identification and confirmation of target compounds in environmental samples is rarely an easy task. The judgement and experience of the analyst and his/her colleagues is an important part of the evaluation of chromatographic data. The analyst should ask:

- is there previous data or current information about the sample that would aid in evaluating the data?
- do the peaks look normal?
- are the integrations correct?
- are there coeluting peaks or matrix interferences?

11.1 Qualitative analysis

Identification of the target compounds is based on retention time of the target compound and its relative retention time compared to the internal standard. A default window of 0.10minutes is recommended for the data system. The analyst will scan the sample chromatogram for the target compounds on the chromatogram and verify that the data system has correctly identified the target compounds, if present. The analyst will use the retention time (RT) of the targets from the previous CCV to identify the target compounds. The analyst should note shifts in the retention times of the internal standard(s) and surrogate compound(s) to help gauge possible shifts in the RT of the target compounds.

It is important to note that the relative retention time (RRT) applies only to peaks that are within the calibration range of the curve. Peaks areas that exceed the established linear range of the calibration curve may result in significant retention time shifts; therefore, all peaks which have significant areas and elute closely to a target compound should be tentatively identified as a target compound and evaluated as such. A dilution is made to bring the area of the peak of interest into the upper half of the calibration curve; that is between the mid-level calibration standard and the highest level standard.

11.1.1 Scan the sample chromatogram for peaks that that correspond to the surrogate compounds. The surrogate compounds should be evaluated first to check for shifts in retention times and to evaluate the surrogate recovery. If the data system has identified a peak as a surrogate, the analyst will verify that the selected peak is properly identified and that the quantitation is reasonable.

The sample is spiked with two surrogates: a,a,a-trifluorotoluene (PID and FID) and bromochloromethane(HECD). The recovery criteria are given in Section 5 of the SL QAPs.

NOTE: If the recovery of the surrogate(s) is above (the recovery exceeds the upper control limit) the acceptance criteria and no target compounds are detected in the sample, results may results may be reported if the project manager is notified via an NCR.

11.1.2 Scan the sample chromatogram for the presence of peaks that corresponds to a target compound and verify that the data system has properly identified the target compound and has calculated a reasonable concentration for the target. The analyst should observe the general appearance of the chromatogram for possible dilutions, matrix interferences, the presence of multi-response peaks(e.g., gasoline) and the overall shapes of the peaks.

If the concentration is below the detection limit, the reporting limit(RL) for that compound is calculated(Section 11.2). The RL is calculated for all target compounds that are not detected on the primary analytical column. Peaks that are erroneously designated by the data system as a target compound must be marked as undetected by the analyst and proper identification assigned.

If the concentration of the target compound exceeds the calibration range, the sample must be diluted to bring the concentration of the target compound into the upper half of the calibration range; that is between the mid-level calibration standard and the highest level standard.

NOTE: If a peak is detected on the primary column at a concentration that exceeds the calibration range, it may be advantageous to evaluate the confirmation column prior to analyzing the dilution. If no peak is detected on the conformation column or if the concentration of the corresponding peak is within the calibration range, the analysis of the dilution may not be necessary.

11.1.3 It is the policy of SL not to routinely confirm VOC on a second column. The purge and trap sample preparation eliminates many matrix interferences and the use of selective detectors such as the HECD and PID provide sufficient information to qualitatively identify a target compound. Second column confirmations for VOC by GC are provided only at client request or if required by regulatory agency. If second column confirmation is required, the following steps are followed:

11.1.4 If the result for a target compound is above the reporting limit(RL) on the primary column, the sample is analyzed on the confirmation column at the highest dilution analyzed on the primary column. The analyst will use the relative retention time (RRT) window calculated using the CCV as guidance for the identification of the target compounds. The analyst should also note shifts in the retention times of the surrogate compounds to help gauge possible shifts in the RT of the target compounds.

Scan the chromatogram on the confirmation column for peaks that correspond to target compounds tentatively identified on the primary column. Targets that are not detected on the primary column do not require confirmation. The analyst should observe the general appearance of the chromatogram for possible dilutions, matrix interferences, the presence of multi-response peaks, and the overall shapes of the peaks. If the concentration of the target compound on the confirmation column is below the quantitation limit, the RL for that compound is calculated and the peak corresponding to the tentatively identified compound on the primary compound is documented as "not confirmed."

If the target compound is detected on the confirmation column, the concentration of the target compound is calculated and compared to the result from the primary column. The relative percent difference is calculated:

$$\%RPD = \left| \frac{(Cprim - Cconf)}{\frac{(Cprim + Cconf)}{2}} \right| \otimes 100$$

where
Cprim = concentration of the target compound on the primary column
Cconf = concentration of the target compound on the confirmation column

If the relative percent difference is less than 40%, the presence of the target compound is confirmed and the lowest concentration is reported.

NOTE: Since EPA has switched to %RPD, some judgement will be required to determine whether to report a result as a quantitative result. (The relative percent difference between any two numbers will be a maximum of 200%). A large relative percent difference may be acceptable at concentrations near the reporting limit. If in doubt about whether to report a peak as a quantitative result, consult the section supervisor.

If the %RPD is greater than 40%, the chromatograms are evaluated to determine if matrix (non-target) interferences are present on one or both columns. If the interference can be explained, the analyst should report the lowest result and flag the result to note the disparity between the results. If the disparity cannot be explained, the analyst should attempt to confirm the results by GC/MS (if the concentration is high enough). If the result cannot be conformed by GC/MS, report the lower result and flag it accordingly. Alternatively, dilute the extract to a level that removes the interference and report the RL from this dilution.

The following table summarizes the general guidance for the evaluating of chromatographic data. The table assumes that the calibration criteria has been met and that the sample has acceptable associated surrogate and lab spike recoveries.

PEAK INFORMATION	ACTION	REPORT*
No peaks detected on primary or secondary column		Report < RL
Peak found at RRT on primary column	Peak is tentatively identified as the target	-If concentration < RL, report < RL -If concentration > RL, evaluate confirmation column.
Peak detected at RRT of target on confirmation column	Peak is confirmed as the target	-If concentration < RL, report <RL -If concentration >RL, calculate %RPD -if %RPD <40%, report lowest concentration of primary and confirmation analyses. -if %RPD >40%, report concentration that is most reasonable and flag result to note the disparity Case narrative or note to PM may be required for complex matrices.

*RL may be the SL Reporting Limit in Table 5 of the CQAP or may be defined by the client QAP or contract.

The analyst must clearly show how the reported sample results were determined. False hits identified as targets by the data system should be documented as 'non-detects" on the quantitation report. Manual calculations and integrations must be documented and available for inspection.

11.1.4 Identification "Tools"

11.1.4.1 The retention time of a surrogate compound provides useful information about the stability of the GC system. If the surrogate RT has not changed, it is probable that the target analytes RTS have not changed. The relative retention time can help the analyst to evaluate a peak:

$$RRT = \frac{RT_{target}}{RT_{surrogate}}$$

The relative retention time ration will remain fairly constant under the same GC conditions. That is, if the absolute retention time of the reference changes, the target should have a corresponding change. The "expected retention time of the target can be estimated from the RRT and the RT of the reference (in this case, the surrogate):

$$RT_{target} = RRT \ x \ RT_{surrogate}$$

If the absolute RT of the reference increases, one would expect the RT of the target to increase; if the RT of the reference decreases, one would expect the RT of the target to also decrease.

The analyst must be alert for the presence of matrix interferences and the evaluate the data on both columns before making an identification.

Another useful "tool" is to add a known amount of the target analyte to a portion of the extract. The analysis of this "fortified extract" may provide chromatographic information that supports or refutes the initial identification. The analyst is cautioned to use this approach with discretion and with consultation with the GC supervisor. As a general rule, spike a portion of the extract with an amount of target analyte that will result in about a 2-fold increase in response.

NOTE: Do not perform this procedure until you have exhausted other avenues and have consulted with the GC supervisor or other manager with GC experience.

11.2 Calculations for Samples-Internal Standard Technique

11.2.1 Aqueous Samples

If a regression curve is used, the concentration is given:

$$concentration(ug/L) = concentration(curve) \otimes DF$$

where
DF = dilution factor

If the relative response factor is used, the calculation for samples is :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes DF$$

where
Ax = area of the target compound being measured
Ais = area of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
DF = dilution factor

The reporting limit (RL) for each sample is given:

$$RL(ug/L) = RLqap \otimes DF$$

where
DF = dilution factor. The SL CQAP Table 5 RL(RLqap) assumes a DF of 1.

11.2.2 Soils by Heated P/T

If the regression curve is used, the concentration is given:

$$conc(ug/kg, dw) = Ccurve(ug/kg) \otimes \frac{5.0g}{(W)(solids)}$$

where
Ccurve = concentration from curve(ug/kg)
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100

If the relative response factor is used, the calculation for samples is :

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{5.0g}{(W)(solids)}$$

where
Ax = area of the target compound being measured
Ais = area of the internal standard
Cis = concentration of the internal standard (ug/kg)
RRFavg = average response factor of the compound being measured
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The LQM assumes W= 5.0g and solids = 1.

11.2.3 Methanol Extraction Soils and Wastes

If the regression curve is used, the concentration is given:

$$conc(ug,kg,dw) = Ccurve(ug/L) \otimes \frac{Vcal}{(W)(solids)}$$

where
Vcal = volume that calibration curve is based on (0.005L or 0.025L)
W = weight of sample added to the reagent water (g)-defined above(11.2.3.1)

If the relative response factor is used, the calculation for samples is :

$$concentration(ug/kg,dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{Vcal}{(W)(solids)}$$

where
Ax = area of the target compound being measured
Ais = area of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = (percent solids)/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

The reporting limit (RL) for each sample is given:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the reagent water (g)
solids = (percent solids)/100)

The LQM assumes W= 5.0g and solids = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The **analytical batch** consists of up to twenty client samples and the associated QC items that are analyzed together. The QC items for an analytical batch consist of a method blank, a lab control standard(LCS), a lab control standard duplicate(LCSD), a matrix spike(MS), and a matrix spike duplicate(if there is sufficient volume to perform the MS/MSD). Note that the method blank for liquid samples and low level soils is clock-specific and that the method blank for medium level soil samples is batch-specific.

SL-SOP AN02: *Analytical Batching* describes the procedure for evaluating batch-specific QC. This criteria is summarized in the attached SOP Summary.

See SL SOP AN02 for the calculations of theoretical concentrations spikes, accuracy, and precision.

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must demonstrate competence in the analysis of samples by this procedure. The minimum requirement for this demonstration is the preparation and analysis of spiked reagent water. Section 8 of SW-846 Method 8000B give the general procedure for the performance of the IDOC.

12.3 Method Detection Limit

The method detection limit is determined by each lab annually in accordance with SL SOP CA90:*Procedures for the Determination of Method Detection Limit(MDL).*

13.0 PREVENTIVE MAINTENANCE AND TROUBELSHOOTING-no items in this revision

14.0 WASTE MANAGEMET AND POLLTUION PREVENTION

Excess reagents, standards, and samples must be disposed in accordance with SOP CA70: Waste management.

15.0 REFERENCES

Test Methods for Evaluating Solid Waste, Third Edition; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC. (Update III)

8021B METHOD SUMMARY

HOLD/STORAGE
Container: Aqueous: 40mL vial with Teflon-lined cap, no headspace Soil: Pre-weighed vial 40mL vial; a separate sample is also collected in a 40mL or 125mL vial for "dilutions", if required.
Preservative: Aqueous: If chlorine is present, add ascorbic acid (25mg per vial)
Soils: No field preservative required for bulk and Encore samples. Encore must be transferred to a storage vial within 48 hours of collection and preserved with sodium bisulfate or frozen in water.
Storage: 4C (less than 6C with no frozen samples)
Hold Time: Aqueous:14 days if preserved at collection with HCl to pH<2; 7 days if unpreserved.
Soils:14 days if preserved within 48 hours of collection

ANALYSIS
Aqueous/methanolic extract: ambient
Soils: heated, 40C
Wastes: methanol extraction followed by ambient or heated P/T
Calibration standards and samples at same volume/weight

ANALYTICAL SEQUENCE

Analysis of Initial Calibration Standards
Analysis of Method Blank
Sample analyses-8021 until 12-hour clock expires;
Continuing Calibration Verification Standard-8021: every 12 hours
Analysis of RL Standard-lowest level calibration standard
Analysis of Method Blank
Sample analyses-8021 until 12-hour clock expires

The analytical clock for 8021 is 12 hours. The clock starts at the injection of the first calibration standard or CCV. The sequence continues until all samples have been analyzed or until the CCV fails the acceptance criteria.

SURROGATE(S):
Bromochloromethane- (aqueous)-10ug/L; (soils)-50ug/kg
a,a,a-Trifluorotoluene- (aqueous)-30ug/L; (soils)-150ug/kg

INTERNAL STANDARD(S):
4-Bromofluorobenzene- (aqueous)-30ug/L; (soils)-150ug/kg

BATCH QC
LCS/LCSD- CQAP subset at 20ug/L(aqueous); 100ug/kg(soils)
MS/MSD- CQAP subset at 20ug/L(aqueous); 100ug/kg(soils)

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Initial Calibration- 5 point minimum with lowest point at or below the RL	Prior to sample analyses or when CCV fails	1) RSD of each target <= 20%; OR 2) plot regression curve CC>=0.99 for each target	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Continuing calibration verification(CCV)	Every 12 hours prior to method blank and samples	+/-15% drift or difference; +/-20% for gases and polar compounds	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Method blank	After CCV Method blank must be analyzed prior to the analyses of samples	Targets < RL	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SL SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze
Lab control sample (LCS)	Per batch or twenty or fewer samples (see SL SOP AN02)	Recoveries within SL CQAP Section 5 limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SL SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix spike(MS) and matrix spike duplicate (MSD)	At a frequency of 5% of samples or as requested (see SL SOP AN02)	Recoveries within SL CQAP Section 5 limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SL SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze
Surrogates	All samples, method blanks, and QC	Recoveries within SL CQAP Section 5 limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SL SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze
Internal standard area	Evaluate each sample, blank, QC item	+/- 2X ISTD of area in CCV	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Reporting limit standard- standard at 1-2X the RL; used to verify the sensitivity of the system	Daily(optional) (see specific state requirements for frequency)	Detected at reasonable response	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard -Remake and reanalyze standard -Perform system maintenance and recalibrate
Initial demonstration of Capability(IDOC)-the analyst has to perform the IDOC for either of the analogous 600 or 8000 series methods, not both.	Per analyst	Within the 600-series method criteria	-Reanalyze QC sample for the targets that failed to meet the criteria
Method detection limit(MDL)	Annually	Evaluate data using SL SOP CA90	Evaluate data using SL SOP CA90

**the same second source standard material is used for the calibration verification, the LCS/LCSD, and the MS/MSD.*

TABLE 1 - TARGET COMPOUNDS

Routine Target Compounds - Hall Electrolytic Conductivity Detector (HECD)

Target Compound	Retention Time(min)
Dichlorodifluoromethane	4.83
Chloromethane	5.54
Vinyl chloride	5.74
Bromomethane	6.77
Chloroethane	7.11
Trichlorofluoromethane	7.94
1,1-Dichloroethene	9.55
Methylene chloride	11.05
t-1,2-Dichloroethene	11.87
1,1-Dichloroethane	13.14
c-1,2-Dichloroethene	47.88
Bromochloromethane(S)	15.59
Chloroform	15.84
1,1,1-Trichloroethane	16.34
Carbon tetrachloride	16.83
1,2-Dichloroethane	17.52
Trichloroethene	19.40
1,2-Dichloropropane	20.08
Dichlorobromomethane	20.96
2-Chloroethyl vinyl ether	21.92
c-1,3-Dichloropropene	22.34
t-1,3-Dichloropropene	24.10
1,1,2-Trichloroethane	24.68
Tetrachloroethene	25.103
Dibromochloromethane	25.95
Chlorobenzene	27.91
Bromoform	30.69
4-Bromofluorobenzene(I)	31.78
1,1,2,2-Tetrachloroethane	32.31
1,3-Dichlorobenzene	35.53
1,4-Dichlorobenzene	35.84
1,2-Dichlorobenzene	37.15

Additional Compounds-HECD

Target Compounds	Retention Time(min)
Bromochloromethane(S)	15.70
Dibromomethane	20.64
1,2-Dibromomethane	27.94
1,1,1,2-Tetrachloroethane	28.27
4-Bromofluorobenzene(I)	31.87
Bromobenzene	32.50
1,2,3-Trichloropropane	33.03
2-Chlorotoluene	33.23
4-Chlorotoluene	33.39

TABLE 1 - TARGET COMPOUNDS

Routine Target Compounds- Photoionization Detector (PID) or Flame Ionization Detector(FID)

Target Compound	Retention Time(min)
Methyl t-butyl ether(MTBE)	8.57
Benzene	14.45
a,a,a-Trifluorotoluene(S)	16.62
Toluene	20.24
Chlorobenzene	24.94
Ethylbenzene	25.22
m,p-Xylene	25.50
o-Xylene	26.91
Styrene	27.00
4-Bromofluorobenzene(I)	28.92
1,3-Dichlorobenzene	32.69
1,4-Dichlorobenzene	33.06
1,2-Dichlorobenzene	34.28

Additional Compounds-FID

Target Compounds	Retention Time
Diethyl ether	6.17
Acetone	6.56
Hexane	9.27
2Butanone (MEK)	11.30
Heptane	14.58
a,a,a-Trifluorotoluene(S)	16.72
4-Methyl-2-pentanone(MIBK)	18.42
2-Hexanone	21.59
4-Bromofuorobenzene(I)	29.00

SEVERN TRENT SERVICES

VOLATILE COMPOUNDS BY GC/MS (EPA 8260B)

Approved by:

[signature] 3 April 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures that can be used to determine the concentration of volatile organic compounds (VOC) in water, wastewater, soils/sediments, wastes, oils, sludges, and solids. The attached quantitation report lists the target compounds, an example of the retention time order of each target compound, the quantitation and confirmation ions of the target compounds, and internal standard assignments.

1.2 The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision criteria for each target compound are listed in Section 5 of the current revisions of the STL Laboratories' *Comprehensive Quality Assurance Plan* and *Corporate Quality Assurance Plan.*

2.0 SUMMARY OF METHOD

2.1 Volatile organic compounds (VOC) are purged from the sample matrix with helium. The VOC are transferred from the sample matrix to the vapor phase. The vapor is swept through a sorbent tube where the VOC are trapped. After the purging is completed, the trap is heated and backflushed with helium to desorb the VOCs onto a GC column. The GC is temperature-programmed to separate the VOC, which are then detected by a mass spectrometer. Qualitative identification of the target compounds in the sample is based on the relative retention time and the mass spectra of the characteristic masses (ions) determined from standards analyzed on the same GC/MS under the same conditions. Quantitative analysis is performed using the internal standard technique with a single characteristic ion.

2.2 Aqueous samples may be purged at ambient conditions (recommended) or at 40C (optional). Five to twenty-five milliliter aliquots of the sample may be purged. The calibration standards and the associated QC must be analyzed under the same conditions and volume.

2.3 Low-level (nominally <1mg/kg) soil samples are purged at 40C in a purge and trap instrument designed to add water and internal standards to the vial containing the sample without breaking the seal. The sample is stirred during purging to thoroughly mix the soil and water. The calibration standards are purged under the same conditions.

2.4 High level soils (nominally >1mg/kg) and waste samples are extracted with methanol-1mL of methanol per gram of sample. An aliquot of the methanol extract is injected into reagent water. The methanol extract/reagent water is purged at ambient temperature using the same instrument conditions and calibration used for aqueous samples.

2.5 This method is based on the guidance in SW-846 Methods 8260B and 5035.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put yourself or others in a potentially hazardous situation.

3.2 Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, eye protection, or other equipment should be used. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst at each lab division. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

3.4 The exit vent of the split injector must have a carbon trap in-line to collect the volatile compounds that are vented during the injection of the sample. The traps should be changed a minimum of every three months and disposed of in accordance with STL-SL SOP CA70: *Waste Management.*

4.0 INTERFERENCES

4.1 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.2 The volatiles lab must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator blanks should be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in STL-SL SOP AN70: *Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

4.3 Matrix interferences may be overcome by the use of the secondary ions for quantitation. An example of this is the use of mass 82 for quantitation with chlorobenzene-d5 internal standard when a potential co-eluter, 1,1,1,2-terachloroethane, is a target compound. One of the mass fragments of 1,1,1,2-tetrachloroethane is mass 117, which is the recommended quantitation ion for chlorobenzene-d5. The use of the secondary ions should be used for quantitation in such cases when the lab can clearly demonstrate matrix problems. Mass 58 is recommended for quantitation of acetone due to the elution of a hydrocarbon at the same retention time.

4.4 The analysis of highly contaminated samples (>1mg/L or >1mg/kg) can affect succeeding analyses. Carry-over can occur when low concentration samples are analyzed after high concentration samples. Trap replacement and purging of the entire purging system may be necessary when carry-over is suspected. Reagent blanks must be analyzed when carryover is suspected to demonstrate that the system is free from contamination.

4.5 The Teflon seals of the purge and trap device can absorb and outgas many of the compounds that are included in this method. These Teflon fittings should be periodically checked for integrity. If contamination of the fittings is suspected, the fittings may be heated at 105 C for one hour or replaced.

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquid samples are collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are acidified at the time of collection with about 0.10mL of concentrated HCl per 40mL of sample. The acid prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The sample must be iced at the time of collection and refrigerated at 4C (less than 6C with no frozen samples) in the lab until analysis.

Check each sample vial at the time of receipt for the presence of "bubbles". If the bubbles are less than 3mm in diameter, the vial is acceptable. If the bubble is greater than 3mm, use another vial. Notify the department supervisor or project manager if there are no acceptable vials for analysis.

A "sacrificial" vial or the vial used for screening analysis is used to check the sample pH. If the sample pH is greater than 2, notify the department supervisor or project manager. If directed by supervisor or project manager, hydrochloric acid may be added through the septum to bring the pH <2. Do not add more than 400uL (0.40mL) of 1:1 HCl to a VOC vial. If pH cannot be adjusted to <=2 without destroying the integrity of the sample, the sample must be analyzed within 7 days of collection.

The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for un-preserved samples is 7 days.

5.2 Soils: Soils are routinely collected in duplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with a Teflon-lined cap. The bulk sample can be used for the methanol extraction if the concentration of the sample collected in the Encore exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be transferred within 48 hours of collection to sealed vials containing sodium bisulfate solution or methanol. If the sample contains high levels of carbonates, the sample is preserved with water and frozen until the time of analysis. The procedure for preparing soil samples is given in Section 9.2.

The hold time of the preserved sample is 14 days from the date of collection. The hold time for frozen samples is 14 days from the date of collection.

5.3 High level soil and waste samples are collected in glass containers (usually 125-mL clear glass) equipped with Teflon-lined caps. Soil samples may also be submitted as core samples contained in Encore samplers, metal or plastic "tubes", or in 40-mL VOA vials. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples). The holding time for soil and waste samples subjected to methanol extraction is14 days from date of collection; that is, the extraction and analysis must be completed within 14 days of collection.

5.4 TCLP leachate samples are collected with no headspace in Tedlar bags or syringes. The leachate samples are acidified at the time of collection (after the leaching procedure) with about 0.10mL of concentrated HCl per 40mL of sample and stored at 4C (less than 6C with no frozen samples) from the time leaching is completed until the analysis. The acidified leachate sample must be analyzed within 14 days of the leaching procedure. If the sample is not acidified, the leachate must be analyzed within 7 days of the leaching procedure.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See STL-SL SOP AN70. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

The apparatus and materials listed in this section may vary from lab to lab. The items listed are to give guidance and to provide a general overview of the equipment employed in this analysis.

6.1 Mass spectrometer: equipped with a capillary direct interface and a split/splitless injector or molecular jet separator

6.2 Gas chromatograph, compatible with the MS and purge and trap systems. If the GC is equipped with an injector that is operated in the split mode, the exit vent must have a carbon trap in-line to collect the volatile compounds that are vented during the transfer from the purge and trap device. The carbon traps should be changed a minimum of every three months.

6.3 Purge and trap device Tekmar 3000 Liquid Concentrator or equivalent

6.4 Supelco Vocarb 3000 trap or equivalent, Other traps may be used as long as the target compounds can be detected at the required quantitation limit.

6.5 Archon soil analyzer for low level soils, compatible with Tekmar purge and trap instruments. The instrument must be capable of automatically adding water and internal standard to the container while maintaining the septum seal, heating the sample to 40C, and spinning the stir bar to mix the sample during the purging step.

6.5 Data System compatible with the analytical system

6.6 Microsyringes: 10ul, 25ul, 50ul, 100ul, 250ul, 500ul, 2.5mL

6.7 Gastight syringe: 5mL, 25mL with luerlock tip

6.8 Volumetric flasks: 1.0mL, 10mL, 100mL

6.9 Recommended Columns

J&W DB-624: 60m x 0.32mm ID, 1.8um film
J&W DB-624: 20m x 0.18mm ID, 1.8um film

7.0 REAGENTS

Reagents must be tracked in accordance with STL-SL SOP AN44: *Reagent Traceability.*

7.1 Reagent water-free of volatile contaminants (obtained by purging with inert gas or carbon filtration)

7.2 Methanol-Burdich and Jackson, Purge and Trap grade

7.3 Sodium bisulfate-reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Soil preservation solution- Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC-especially water-soluble solvents such as acetone. The reagent should be tested prior to use by the analysis of a blank containing 5mL of the solution. The reagent is acceptable if it meets the same criteria as a method blank.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with STL-SL SOP AN41: *Standard Material Traceability.*

8.1 Preparation of **Stock Standards** from Neat Compounds

The lab should attempt to obtain a certified primary standard or secondary standard before preparing stock standards from neat materials. If primary stock standards must be prepared in-house, the target concentration range is from 2000ug/mL to 10000ug/mL. SL-SOP AN43: *Standard Preparation* gives the general instructions for the preparation of the stock solutions from neat materials.

8.2 Preparation of the **Working Standard** from Stock Standards

The working standard is prepared from the primary stock standards that are either prepared from neat compounds or purchased as certified solutions. The working standard contains one or more of the target compounds at a concentration suitable for preparing the calibration standards, generally 10-200ug/mL. A known volume of the working standard is then added to a known volume of reagent water to make the calibration standard.

The standards and standard concentrations listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document the standard preparation procedures in the standard traceability log.

8.3 Preparation of the **Calibration Standards** from the Working Standards

The calibration standards are the standards that are analyzed on the instrument. The calibration standard is made by adding a known volume of the working standard to a known volume of reagent water. The instrument must be calibrated using a minimum of five calibration standards. The lowest level standard must be at the reporting limit and the rest of the standards will define the working range of the analytical system.

8.3.1 Add 5.0mL of reagent water to a 5mL-glass syringe or 25ml of reagent water to a 25-ml glass syringe.

8.3.2 Add a known volume of the working standard to 5.0mL or 25ml of reagent water.

NOTE: The calibration standards for the low level soils are prepared using the same procedures as for the 5mL water purge except that the standards are purged at 40C. The lab has the option of using blank sand in the calibration standards.

The calibration standards listed in Table 1 are the suggested for routine use. If other "recipes" are used, the lab must document these standard preparation procedures in the standard traceablity log. A 5mL-purge volume may be used for low level (nominal RL of 1ug/L) if the instrument has sufficient sensitivity to detect the targets and the calibration criteria is met.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance provided in STL-SL-SOP AN70.

9.1 **Aqueous samples** are analyzed directly by purge and trap/GC-MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded prior to analysis to determine if the sample has been properly preserved.

9.2 Preparation of Soil Samples (5035)

9.2.1 Remove the Encore samples and the bulk sample from the storage area.

9.2.2 Test an aliquot of the bulk sample for the presence of carbonates.

- Transfer 5g of sample from the bulk sample to a 40mL vial..
- Add 5ml of the sodium bisulfate solution and shake the vial .
- If the sample exhibits effervescence, the Encore samples should be preserved as described above using 5mL of volatile-free water in place of the sodium bisulfate solution and placed in a freezer at –10C. The analytical hold time for frozen samples is 14 days from collection.
- If no effervescence is noted, the Encore samples may be preserved with 5mL soil preservation solution.

9.2.3 Add a stir bar to a vial and weigh the vial and record its tare weight(or tare the vial and stir bar weight by pressing the autotare button).

9.2.4 Transfer the sample from the Encore sampler to the tared vial and record the weight of the sample log.

If the sample effervesced during the carbonate test (9.2.2), add 5.0mL of reagent water and freeze at –10C.
The hold time is 14 days from collection.

If not, add 5.0mL of the soil preservation solution, seal the vial, and store the sample at 4C until the time of analysis. The preserved sample must be analyzed within 14 days of collection.

NOTE: A preparation blank is prepared when Encore samples are transferred. The preparation blank contains the same reagents as the samples-either 5mL of reagent water or 5mL of soil preservation solution.

9.3 A methanol extraction is prepared when the concentration of the target compounds (by direct purge) exceeds the working range of the calibration curve. The bulk sample, collected in the 125-mL sample container, can be used to prepare the methanol extraction. Carry out the preparation quickly to minimize the loss of volatiles.

-Mix the sample with a stainless steel spatula and transfer 10g (+/- 0.5g) to a glass vial.

-Add 8uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 10g and 100% percent solids, is calculated:

$$Ct(ug/kg, dw) = \frac{0.008mL \otimes 2500ug/mL}{0.010g \otimes solids} = 2000ug/kg, dw$$

-Shake the sample for two minutes. Allow the solvent to separate from the solids portion of the sample and transfer a 1-2mL aliquot of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

-For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The lab control standard is prepared by adding 8uL of the surrogate spiking solution and 8uL of the matrix spiking solution to 10mL of purge and trap grade methanol. Assume a sample weight of 10g. Analyze 125uL of the extract.

The matrix spikes are prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) and 8uL of the matrix spiking solution (2500ug/mL) to 10-g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for two minutes. Analyze 125uL of the extract or a smaller volume if the VOC concentration is high.

-Add 125uL of the extract (or a smaller volume if the VOC concentration exceeds the linear range of the system with 125uL) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

9.4 Methanol Extraction for Wastes

Carry out the preparation quickly to minimize the loss of volatiles.

9.4.1 Mix the sample with a stainless steel spatula and transfer 1g (+/- 0.2g) to a glass vial.

9.4.2 Add 10uL of the surrogate spiking solution (2500ug/mL) to the sample and quickly add 10mL of purge and trap grade methanol. If the sample is completely soluble in the methanol, dilute to a final volume of 10mL. The theoretical concentration of the surrogates in the sample, assuming a sample weight of 1.0g, is calculated:

$$Ct(ug/kg) = \frac{0.010mL \otimes 2500ug/mL}{0.0010g \otimes solids} = 25000ug/kg$$

9.4.2 Shake the sample for one minute. Allow the solvent to separate from the solids portion of the sample and transfer 1mL to 2mL of the extract to a storage vial. The vial should be sealed with no headspace. Store the methanol extract at 4C until the time of analysis. The extract must be analyzed within 14 days of sample collection.

For each batch of twenty or fewer samples, prepare a method blank and a lab control standard. Prepare a matrix spike and matrix spike duplicate at a frequency of 5% of all samples.

The method blank is prepared by adding 8uL of the surrogate spiking solution (2500ug/mL) to 10mL of purge and trap grade methanol. Assume a sample weight of 1.0g. Analyze 100uL of the extract.

The lab control standard is prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 5.0mL of purge and trap grade methanol. Assume a sample weight of 5.0g. Analyze 100uL of the extract.

The matrix spikes are prepared by adding 10uL of the surrogate spiking solution (2500ug/mL) and 10uL of the matrix spiking solution (2500ug/mL) to 1g aliquots of the sample selected for the MS/MSD. Quickly add 10mL of purge and trap grade methanol to each sample and shake for one minute.

Add 100uL of the extract (or a smaller volume) to 5.0mL of water (or to 25mL if the calibration is based on 25mL). Add the internal standard solution and analyze the sample using the ambient water calibration.

NOTE: Waste samples may require significant dilution prior to analysis.

10.0 PROCEDURE

The following instrument conditions are recommended. The actual conditions may vary due to differences in instrumentation. The lab must document the instrument conditions in the maintenance log, the data system, or on the analysis log.

10.1 Instrument Conditions

10.1.1 GC Conditions
GC conditions may vary according to the environment and condition of each instrument. The lab must document the instrument conditions to assure consistent results and to aid in trouble-shooting the analytical system. Each lab is responsible for assuring that the conditions necessary to achieve adequate separation and sensitivity of the target analytes are maintained.

10.1.1.1 Example GC temperature program

Initial column temperature: 35 C for 3 minutes
Column temperature program 1: 20C per minute
Intermediate column temperature: 70C for 4 minutes
Column temperature program 2: 10C per minute
Final column temperature: 200C for 5.25 minutes

10.1.1.2 Column flow: Approximately 5-10mL/minute helium with a make-up of 20-25mL/minute helium. Total flow into the jet separator should be about 30mL/minute. The vacuum gauge on the jet separator will read about 0.5Torr.

If no jet separator is used and the column is plumbed directly into the source, the column flow should be adjusted to 0.5-1.0ml/min and a split ratio (desorb to column flow) of about 40:1 established. Smaller bore capillary columns (0.18 to 0.32mm) are required if the column is plumbed directly into the source

10.1.1.3 Mass Spectrometer and interface parameters

Jet separator temperature: 240C
Mass spectrometer interface: 240C
Mass spectrometer source temperature: factory set at 300C
range: 35-300amu, with a minimum scan cycle of 1 scan per second

10.1.2 Purge and Trap Conditions
The purge and trap conditions listed in this section are for guidance. The lab must document the actual conditions used. The purge time must be 11 minutes. Other parameters may be varied to optimize the detection of the target compounds.

10.1.2.1 "Three ring trap"-charcoal, Tenax, silica gel
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 180C
Bake time: 8 minutes at 225C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

10.1.2.1 VOCARB 3000 trap
Purge Time: 11 minutes
Purge temperature: aqueous-ambient; soils-heated 40C
Desorb time: 4 minutes
Desorb temperature: 225C
Bake time: 8 minutes at 250C
Purge flow: Approximately 20-30mL/minute
Valve temperature: 100C
Transfer line: 100C

The purge flow must be balanced for adequate sensitivity of the target compounds. If the purge flow is too high, the response of the gases will be low and not reproducible. The SPCC criteria for chloromethane may not be achieved if the purge flow is too high. If the purge flow is too low, the response of the more water-soluble targets-ketones, ethers, bromoform-may be low and the reporting limit may not be achieved on a routine basis.

10.2 BFB Tune Check

10.2.1 Fifty nanograms of 4-BFB must be analyzed at the beginning of each 12-hour clock as a check on the "tune" of the mass spectrometer. Meeting the tuning criteria ensures that the instrument is measuring the proper masses in the proper ratios. The 4-BFB analysis takes place under the same instrument conditions as the calibration standards and samples except that a different temperature program can be used to allow for the timely elution of 4-BFB. All other instrument conditions must be identical-the mass range, scan rate, and multiplier voltage. If the instrument is configured for direct injection, 50ng of 4-BFB may be injected directly on to the column. If the purge and trap is used to analyze the 4-BFB, the purge and trap conditions must be the same as for the calibration standards and samples.

10.2.2 Evaluation of the 4-BFB peak.

10.2.2.1 The chromatogram should exhibit acceptable baseline behavior and the 4-BFB peak should be symmetrical. A spectrum of the baseline that shows high abundances of mass 40 (Argon) and mass 44 (carbon dioxide) may indicate a leak or contaminated carrier gas.

10.2.2.2 The spectrum of the 4-BFB must meet the criteria listed in the attached SOP Summary. Background subtraction must be straightforward and designed only to eliminate column bleed or instrumental background. Scans +/- 5 scans from the apex can be evaluated for the 4-BFB criteria. Consecutive scans within this range can be averaged to meet the criteria.

10.2.2.3 The following records must be kept for each 4-BFB analysis that meets the criteria:
- the date, time, and data file of the analysis
- a spectrum of the scan or averaged scans
- a tabulation of the ion abundances of the scan

10.2.2.4 The 4-BFB analysis should be evaluated as to the relative size of the 4-BFB peak under the m/z 95 profile. A benchmark area window should be established for each instrument. Response outside of this window suggests instrumental problems such as a poor purge, clogged jet separator, leak in the Tekmar purging device, reduced or elevated detector sensitivity, improper electron multiplier voltage selection, wrong tune method or tune file selected for this analysis, PFTBA valve left open , or other anomalies.

10.2.2.5 If the 4-BFB fails to meet the acceptance criteria, the instrument may require tuning (manually or automatically with PFTBA). Depending on the nature of the results from the 4-BFB analysis, other corrective measures may include remaking the 4-BFB standard and/or cleaning the mass spectrometer source.

10.3 Initial Calibration

After the 4-BFB criteria has been met, the initial calibration standards are analyzed. Prepare the initial calibration standards according to the example recipes in the SOP appendices or lab-specific recipe. The lab must document the "recipe" used to prepare the calibration standards. The lowest level calibration standard must be at or below the routine RL and the other calibration standards will define the working range of the system.

10.3.1 Remove the plunger from the syringe and fill the barrel to overflowing with reagent water (syringe valve in the "red" position).

10.3.2 Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL or 25mL)

10.3.3 Briefly remove the syringe valve and inject the standards and internal standards into the syringe.

NOTE: Use the internal standard (IST) mix when preparing the calibration standards for analysis. The surrogates are already included in the standard mixes.

10.3.4 Load the standard(s) onto the purge and trap device and begin the analysis. All pertinent information concerning the standards must be recorded on the analysis log. The standards must be clearly identified and traceable to the preparation steps.

NOTE: The standards for low-level soil samples are prepared in the same manner as the 5mL standards. The standards for the low-level soils are purged at 40C. The lab has the option of using blank sand or soil in the calibration standards and the blank in the low level soil analysis.

10.3.5 After the acquisition has taken place, evaluate the calibration standards to ensure that each target compound, surrogate, and internal standard has been correctly identified. The analyst must be careful to complete this step before proceeding.

10.3.6 After each target compound, surrogate, and internal standard has been correctly identified, the relative response factor for each target compound and surrogate is calculated using the data system or using a PC spreadsheet as follows:

$$RRF = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where
Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (see the attached quantitation report for a list of the compounds that are associated with the various internal standards)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug on-column)
Cis = concentration or mass on-column of the internal standard (ug/L or ug/kg OR ng or ug on-column)

The average relative response factor (RRFavg) is calculated for each target compound and each surrogate compound:

$$RRFavg = \frac{RRF1 + RRF2 + ... + RRFn}{n}$$

where n = number of calibration levels

Calculate the standard deviation (SD) for the target compounds and surrogates at all calibration levels:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}(RFi - RFavg)^2}{n-1}}$$

where
Rfi = response factor of a target compound in the individual calibration level
Rfavg = average response factor
n= number of calibration levels

10.3.7 Calculate the relative standard deviation (% RSD) of the calibration levels for each target:

$$\% RSD = \frac{standard\ deviation}{RRFavg} \otimes 100$$

10.3.8 The results of the initial calibration are evaluated against the Calibration Check Compound (CCC) criteria and the System Performance Check Compound (SPCC) criteria, which are listed below. The CCC and SPCC criteria must be met before samples can be analyzed.

Calibration Check Compounds – CCC Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	Continuing Calibration
<=30% RSD	<=20% difference from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

NOTE: The CCC and SPCC criteria must be met even if the calibration curve option is used for quantitation. If the CCC and SPCC criteria do not pass, a new calibration curve must be prepared and analyzed.

10.3.9 After the initial calibration criteria (CCC and SPCC) have been met, each target is evaluated for linearity.

If the %RSD of the target compound is less than or equal to 15%, the average response factor can be used for quantitation of samples.

If the %RSD of the target compound is greater than 15%, a regression curve (linear, quadratic, etc) must be used for the quantitation of samples. A regression curve may also be used for the compounds that have %RSD less than 15%. The results can be used to plot a calibration curve of response ratios-Ax/Ais is plotted on the y-axis; Cx/Cis is plotted on the x-axis where

Ax = area of the characteristic ion for the compound being measured
Ais = area of the characteristic ion for the internal standard associated with the compound being measured (See attached quantitation report for a list of the compounds that are associated with the correct internal standard)
Cx = concentration or mass on-column of the target compound being measured (ug/L or ug/kg OR ng or ug)
Cis = concentration of the internal standard (ug/L or ug/kg OR ng or ug)

If the correlation coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples.. Regression curves may be forced through zero but it is recommended that the curve be evaluated without forcing through zero first and then with the curve forced through the origin. The analyst must ensure that the type of regression curve selected accurately defines the concentration/response relationship over the entire calibration range

When more calibration levels are analyzed than required, individual compounds may be eliminated from the lowest or highest calibration levels(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of the calibration curve be eliminated without eliminating the entire level.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

8000B exception: evaluation of the "grand mean": If the average %RSD of ALL (all targets including CCC and SPCC) compounds in the initial calibration is less than 15%, the average response factor can be used for quantitation of all target compounds. The recommended course is to use regression curves, as described above, to quantify targets where the %RSD criterion (<=15%) is exceeded.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

10.3.10 After the initial calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP or other specified QAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compounds must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of samples can take place.

If the method blank repeatedly fails to meet the criteria, contact the immediate supervisor to determine the cause of the problem and to determine a course of action. This action may include re-cleaning the sparging tubes (with soap, hot water, and methanol), purging the effected autosampler ports with heated methanol, flushing the purge and trap ALS concentrator with methanol, replacing the trap, changing the transfer line, and changing the column. A method blank is then analyzed after taking the corrective action to demonstrate that the contamination has been eliminated. Once the system is determined to be free from contamination, sample analysis may begin. Method blanks may be required after the analysis of samples that contain very high levels of VOC.

10.4 Continuing Calibration Verification

At the beginning of each 12-hour clock, the tune of the instrument must be checked by the analysis of 50ng of 4-BFB. This criteria must be met before the analysis of the calibration check standards can take place.

10.4.1 After the tune criteria has been met, a continuing calibration check standard(s) is analyzed. The continuing calibration standard should be at a nominal concentration of 50ug/L-kg for 5ml/5g samples and 10ug/L for 25mL with ketones and poor purgeables at higher concentrations. The CCC and SPCC criteria (Section 10.3.8) must be met before the analysis of the method blank and samples can take place. The percent difference (%D) is calculated as follows:

$$\%D = \frac{RRFavg - RRFccv}{RRFavg} \otimes 100$$

where
RRFavg = average response factor from initial calibration
RRFccv = response factor from the check (12-hour) standard-calibration verification

The percent drift (%Drift) may also be used to evaluate the change/deviation of the curve:

$$\%Drift = \frac{Ci - Cccv}{Ci} \otimes 100$$

where
Ci = Calibration Check Compound standard concentration
Cccv = measured concentration using the selected quantitation method

NOTE: The SPCC criteria (10.3.8) must be met even if the regression curve option is used for quantitation. If this criteria is not met, corrective action must be taken. The corrective action may include reanalysis of the calibration check standard or preparation of a new secondary stock standard and reanalysis of the calibration check standard. If subsequent analysis of the standard is still out of criteria, a new initial calibration curve must be analyzed and evaluated.

10.4.2 The calibration standard (CCV) must also be evaluated for internal standard retention time and response.

If the retention time of any internal standard changes by more than 30 seconds from the retention times of the internal standards in the initial calibration, the analytical system must be inspected for problems and corrective action instituted.

If the extracted ion current profile (EICP) area for any of the internal standards changes by more than a factor of two (-50% to +100%) from the last calibration check standard, the analytical system must be inspected for problems and corrective action instituted. If the CCV is the first one after the initial calibration, compare the ISTD response to the corresponding level in the ICAL.

10.4.3 After the continuing calibration criteria has been met, the method blank is analyzed. 5.0mL or 25mL of reagent water is spiked with the internal standard/surrogate and analyzed. The concentrations of the target compounds in the method blank are calculated and the results are compared to the reporting limits (RL) in Table 5 of the STL-SL CQAP.

If the concentrations of all target compounds are below the RL, analysis of client samples can take place. Note that all target compound must meet the criteria.

If the concentration of any target compound is above the RL in Table 5 of the STL-SL CQAP, the method blank must be reanalyzed. The analytical system must be demonstrated to be free from contamination before the analysis of client samples can take place.

10.5 Aqueous Sample Analysis-5.0mL to 25mL

The analyst must use the same volume as was used for the calibration standards-if a 5mL sample is used, it must be quanted off of the 5mL calibration curve; if a 25ml sample is used, it must be quanted off of the 25mL calibration curve. Samples are analyzed only after the tune criteria, the calibration (initial or continuing) criteria has been met, and the method blank criteria has been met. See the SOP Summary for the analytical sequence.

10.5.1 Remove the samples to be analyzed from the refrigerator and allow the samples to come to ambient temperature.

10.5.2 Put on a pair of gloves before transferring the sample from the vial to the syringe. The sample is most likely preserved with acid or may contain toxic or hazardous chemicals or biologically active components that may cause skin irritations. ***Gloves must be worn when handling samples.***

10.5.3 Mix the contents of the vial by inverting the vial several times. Check to see if there are air bubbles present in the sample. If air bubbles are present, use another vial if available. Make a note on the analysis log if the sample used contained bubbles and notify the supervisor and/or the project manager.

10.5.5 Remove the plunger from the glass syringe. Attach a syringe valve to the syringe Luer-tip to prevent sample from spilling out of the syringe when sample is added.

10.5.5 Open the vial of the well-mixed sample and gently pour the sample into the syringe barrel. The sample should fill the barrel of the syringe and overflow to allow trapped air bubbles to escape.

10.5.6 Replace the plunger into the syringe barrel. Try not to let air bubbles get into the barrel. If air bubbles are present, turn the syringe up, open the syringe valve , and expel the air while adjusting the volume to 5.0mL or 25mL. If no air bubbles were trapped, adjust the syringe to volume.

NOTE: For TCLP leachate samples, use 1.25mL of sample (1:4 dilution).

10.5.7 Open the syringe valve and inject the internal standard/surrogate (ISSU) mix into the sample.

10.5.8 Transfer the sample from the syringe to the purge and trap device. Record all of the sample identification information on the analysis log. Check the pH of the sample with pH paper and record the pH on the instrument log or other appropriate log.

10.5.9 Analyze the samples using the purge and trap and GC/MS conditions used for the initial and continuing calibration standards.

10.5.10 Determine the concentration of the samples and QC items. If the concentration of a sample is above the highest calibration standard, the sample must be diluted and reanalyzed.

NOTE: Unless otherwise specified by a client QAPP, results from a single analysis are reported as long as the largest target analyte (when multiple analytes are present) is in the upper half if the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client. For TCLP analyses, every reasonable effort should be made to achieve the regulatory level with out instrument overload.

For clients who require we provide lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 of the dilution with t the highest target in the upper half of the calibration curve. For example, if samples analyzed at a 1/50 dilution resulted in a target in the upper half of the calibration curve, the sample would be analyzed at a dilution factor of 1/5 to provide lower RLs.

A dilution is made when a volume of the sample is mixed with the reagent water to a final volume of 5.0mL or 25ml,depending on which curve is being used. The dilution factor is calculated by dividing the volume of sample into the volume used for the calibration curve.

$$DF = \frac{final\ volume\ of\ dilution(mL)}{volume\ of\ sample\ used(mL)}$$

For example, if 1.0mL of sample is diluted to final volume of 5.0mL, the dilution factor is 5. (5.0/1.0 = 5). If 1.0mL of sample is diluted to a final volume of 25mL, the dilution factor is 25 (25/1=25).

The following table gives some dilution factors:

Volume of Sample (mL)	Volume of Reagent Water (mL)	Final Volume (mL)	Dilution factor
5.0	0	5.0	1
2.5	2.5	5.0	2
1.0	4.0	5.0	5
0.5	4.5	5.0	10
0.10	4.9	5.0	50
25.0	0	25.0	1
5.0	20.0	25.0	5
2.5	22.5	25.0	10
1.0	24.0	25.0	25
0.50	24.5	25.0	50
0.10	24.9	25.0	250

NOTE: The same volume of internal standard/surrogate mix (ISSU) is added to the dilution as was added to the undiluted sample.

10.6 Low Level Soil Samples by Heated Purge and Trap (Method 5035)

The soil analytical system is calibrated using the same concentrations as the 5mL purge. The tune, initial and continuing calibration criteria, and the method blank criteria must be met before samples are analyzed. Standards and QC items must be analyzed under the same heated purge and trap conditions.

Remove the samples to be analyzed (Section 9.2) from the refrigerator or freezer and allow the sample to come to ambient temperature. Inspect the vial for cracks or obvious breaches in the septum. Load the samples on to the soil-purging unit and analyze according to the sequence described in Appendix B.

Liquid field QC for soils (trip blank, field blank, etc.) should be analyzed with the associated soil samples, using the same preparation and analytical procedures, including the heated purge. Report the results for liquid trip blanks as ug/L.

10.7 Analysis of Methanol Extracts of Soils and Wastes

The methanol extraction is used when the concentration of one or more target compounds exceeds the linear range of the low-level purge technique (>1000ug/kg). or if the concentration of VOC in the soil or waste samples is high. Samples are analyzed only after the 4-BFB criteria, the calibration criteria (initial and continuing), and the method blank criteria has been met. Medium level soil extracts are quanted using the ambient purge calibration curve. Sample preparation steps are included in Section 9.

10.7.1 Remove the plunger from the 5.0-mL syringe and fill the barrel to overflowing with reagent water(syringe valve in the "red" position). Replace the plunger, switch the syringe valve to "green", and force any airspace out of the syringe. Adjust the volume to the syringe volume(5mL)

10.7.2 Briefly remove the syringe valve and inject the sample extract and 5uL of the internal standard (IST) solution into the syringe. Use 125ul of the extract for soils and 100uL of the extract for wastes. Smaller aliquots are used if the concentration of target analytes exceed the working range of the system.

NOTE: Use the internal standard (IST) mix when preparing the medium level samples. Recall that the surrogates have already been added to the sample during the methanol extraction step (Section 9).

10.7.3 Load the sample on to the purge and trap device and begin the analysis. All pertinent information concerning the samples must be recorded on the analysis log. The samples must be clearly identified and traceable to the extraction log. These conditions must be the same as was used for the initial and continuing calibration standards-ambient purge for aqueous samples.

10.7.4 Determine the concentration of the samples and QC items using the procedures of Section 11. If the concentration of a sample is above the highest calibration standard, a smaller aliquot of the methanol extract is reanalyzed to bring the highest target within the upper half of the calibration curve. Follow the guidelines in Section 10.4.10 for reporting dilutions.

NOTE: It is possible to dilute the surrogates in the sample extract below the linear range of the calibration curve. The minimum extract aliquot that can be used to provide a quantifiable result for the surrogates and matrix spikes is 0.0025mL (2.5uL).

SOIL: 10g to 10mL MeOH	WASTES: 1g to 10mL MeOH	Surrogates- Theoretical ng on-column
125uL(0.125mL)	100uL (0.100mL)	250
62.5uL(0.0625mL)	50uL(0.050mL)	125
25uL(0.025mL)	25uL(0.020mL)	50
12.5uL(0.0125mL)	10ul(0.010mL)	25
2.5uL(0.0025mL)	2.0uL(0.0020mL)	5.0-quantiation limit
<2.5uL(0.025mL)	<2.0uL(0.0020mL)	<5.0ng- below the quantitation limit-diluted out

NOTE: Some instrument quantitation limits may be higher than the limit listed in the table. The volume of extract should be adjusted accordingly.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Qualitative Analysis of Target Compounds

A target compound is identified by the visual comparison of the sample mass spectrum with the mass spectrum of the target compound from a reference spectrum of the target compound stored in a library generated on the same instrument or a standard spectral library such as the NIST/NBS.

11.1.1 Two criteria must be met in order to identify a target compound.

1) elution of the sample component within +/-0.06 RRT (relative retention time) units of the daily standard containing that compound.

$$RRT = \frac{\textit{retention time of the target compound}}{\textit{retention time of the associated internal standard}}$$

2) correspondence of the target compound spectrum and the standard component mass spectrum

11.1.2 All ions present in the standard component mass spectrum at a relative intensity greater than 10% (most abundant ion = 100%) should be present in the sample component mass spectrum. Other ions may be present in the sample component. Coelution of a non-target compound with a target compound will make the identification of the target compound more difficult. These ions due to the non-target compound should be subtracted from the sample component spectrum as part of the background to account for the discrepancy between the sample spectrum and the standard spectrum.

11.1.3 The relative intensities of the ions present in the sample component spectrum should agree within +/- 30% of the relative intensities of the ions in the standard reference spectrum. For example, an ion with an abundance of 50% in the reference spectrum should have a corresponding abundance between 20% and 80% in the sample component spectrum.

11.1.4 If the above criteria are not met exactly, the analyst should seek help from a senior analyst or supervisor. If there is sufficient evidence to support the identification of the component, then the component is identified, quantified, and reported.

11.2 Tentatively Identified Compounds

For samples containing components not associated with the calibration standards, a library search on a reference library, such as the NIST/NBS, may be conducted in order to identify the non-target compounds. Only after visual comparison between the sample spectra and the library-generated reference spectra will the mass spectral analyst assign tentative identification. Tentative identifications of non-targets will be made only by analysts having completed the training specified in the training schedule.

11.2.1 Relative intensities of the major ions (masses) in the reference spectra (ions >10% of the most abundant ion) should be present in the sample spectrum.

11.2.2 The relative intensities of the major ions should agree within +/-30%.

11.2.3 Molecular ions present in the spectrum should be present in the sample spectrum.

11.2.4 Ions present in the sample spectrum but not in the reference spectrum should be reviewed for possible subtraction from the sample spectrum because of over-lapping or co-eluting peaks.

11.2.5 Ions present in the reference spectrum but not in the sample spectrum should be reviewed for possible subtraction from the sample spectrum because of coeluting peaks.

11.2.6 If, in the opinion of the analyst, there is enough evidence to support the tentative identification of a compound even though the above criteria is not met exactly, the peak may be considered tentatively identified. The analyst should consult other analysts or the mass spectral interpretation specialist if there are any questions concerning an interpretation of spectra.

11.2.7 The estimated concentration of the tentatively identified compound (TIC) is calculated using the total ion area of the tentatively identified peak and total ion area of the nearest internal standard that has no interferences. The calculation is

Aqueous

$$TIC(ug/L) = \frac{Cis}{AREAis} \otimes AREAtic \otimes DF$$

where
Cis = concentration of the internal standard, ug/L
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
DF = dilution factor

Soils by Heated P/T

$$TIC\,(ug/kg, dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{5.0g}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
W = weight of sample analyzed, g
solids = decimal equivalent of percent solids

Soils by Methanol Extraction

$$TIC\,(ug/kg, dw) = \frac{Cis}{AREAis} \otimes AREAtic \otimes \frac{Vcal}{(W)(solids)}$$

where
Cis = concentration of the internal standard, ug/kg
AREAis = total ion peak area of the internal standard
AREAtic= total ion peak area of the TIC
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = decimal equivalent of the percent solids(percent solids/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

where
Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

11.3 Calculations for Samples-Internal Standard Technique

Aqueous Samples- relative response factor :

$$concentration(ug/L) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes DF$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
DF = dilution factor

Aqueous Samples: regression curve

$$concentration(ug/L) = concentration(curve) \otimes DF$$

where
DF = dilution factor

The reporting limit (RL) is calculated:

$$RL(ug/L) = RLqap \otimes DF$$

where
DF = dilution factor. The SL CQAP Table 5 RL(RLqap) assumes a DF of 1.

Soils by Heated P/T- relative response factor :

$$concentration(ug/kg, dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{5.0g}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/kg)
RRFavg = average response factor of the compound being measured
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

Soils by Heated P/T: regression curve

$$conc(ug/kg, dw) = Ccurve(ug/kg) \otimes \frac{5.0g}{(W)(solids)}$$

where
Ccurve = concentration from curve(ug/kg)
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The reporting limit (RL) is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the sparging vessel (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

Methanol Extraction Soils and Wastes- relative response factor

$$concentration(ug/kg, dw) = \frac{Ax}{Ais} \otimes \frac{Cis}{RRFavg} \otimes \frac{Vcal}{(W)(solids)}$$

where
Ax = area of the characteristic ion of the compound being measured
Ais = area of the characteristic ion of the internal standard
Cis = concentration of the internal standard (ug/L)
RRFavg = average response factor of the compound being measured
Vcal = volume that calibration curve is based on (5mL or 25mL)
solids = (percent solids)/100)
W = weight of sample added to the reagent water (g)

This weight is determined using the following equation:

$$W = \frac{Wext(g)}{Vf(mL)} \otimes Vext(mL)$$

Wext = weight of sample extracted (g)
Vf = final volume of the extract (mL)
Vext = volume of extract added to the water (mL)

Methanol Extraction of Soils and Solids- regression curve:

$$conc(ug, kg, dw) = Ccurve(ug/L) \otimes \frac{Vcal}{(W)(solids)}$$

where
Vcal = volume that calibration curve is based on (0.005L or 0.025L)
W = weight of sample added to the reagent water (g)-defined above

The reporting limit (RL)is calculated:

$$RL = RLqap \otimes \frac{5.0g}{(W)(solids)}$$

where
W = weight of sample added to the reagent water (g)
solids = (percent solids)/100)

The STL-SL CQAP assumes W= 5.0g and solids = 1.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The analytical batch consists of up to twenty client samples and the associated QC items that are analyzed together. The matrix spike and LCS frequency is defined in Section 3.1.3 of STL-SL SOP AN02: *Analytical Batching*. Note that the method blank for liquid samples and low-level soils is clock-specific and that the method blank for medium level soil samples is extraction batch-specific.

STL-SLSOP AN02: *Analytical Batching* describes the procedure for evaluating batch-specific QC. This criteria is summarized in the attached 8260 SOP Summary.

STL-SL SOP AN02 also contains the calculations for accuracy and precision and the calculations for the theoretical concentrations of surrogates, lab spikes, and matrix spikes.

12.2 Initial Demonstration of Capability (IDOC) to Generate Acceptable Accuracy and Precision

Each analyst must demonstrate competence in the analysis of samples by this procedure. The minimum criteria for this demonstration is the preparation and analysis of spiked reagent water. Section 8.3 of EPA Method 8260A gives the general procedure for the performance of the IDOC and Table 6 of EPA Method 8260A gives the acceptance criteria for the accuracy and precision.

12.3 Method Detection Limit

The method detection limit is determined in accordance with STL-SL SOP CA90.

13.0 PREVENTIVE MAINTENANCE

Preventive maintenance items will be added at a later date. Section 10 of the STL-SL QAPs provide guidance on preventive maintenance.

14.0 TROUBLE-SHOOTING

Trouble-shooting items will be added at a later time. See instrument manufacturers' manuals for guidance on locating and repairing instrument problems.

15.0 REFERENCES

1. *Savannah Laboratories' Comprehensive Quality Assurance Plan* and *Savannah Laboratories' Corporate Quality Assurance Plan*, current revisions.
2. Method s 5035, 8000B, and 8260B. *Test Methods for Evaluating Solid Wastes, Third Edition, SW-846.including Update III* U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

Appendix A

VOLATILES BY GC/MS WORKING STANDARDS -EXAMPLE

These standards can be used to prepare the working standards for EPA Method 8260 to report the TCL (target compound list) compounds and the extended list of target compounds generally associated with EPA 8260. The standards are prepared in purge and trap grade methanol and are stored at 4C with minimum headspace.

Working Standard 1 (TCL WS-1)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #2	2000	12.5	25
VOA Cal #3	2000	12.5	25
VOA Cal #4	2000	12.5	25
1,2,-DCB	5000	5.0	25
1,3-DCB	5000	5.0	25
1,4-DCB	5000	5.0	25
2-CEVE	1000	125	125

Working Standard 2 (TCL WS-2)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA Cal #1	5000	25	125
8260 Surrogates	2500	10	25

Working Standard for GASES (TCL GASES)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
502.2 Cal 1	2000	12.5	25

Appendix A

Working Standard 3 (8260 WS-3)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
8260 Custom Mix #1	200	125	25
8260 Custom Mix #2	200	125	25
1,1,2,2-Tetrachloroethane	2000	12.5	25

Appendix A

Internal Standard (8260 ISTD)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50

Internal Standard/Surrogate (8260 ISSU)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC (ug/mL)
VOA ISTD	2500	20	50
1,2-DCE-d4	2000	25	50
8260 Surrogate	2500	20	50

Tune Evaluation Standard (4-BFB)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
4-BFB	5000	10	50

Matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
Matrix Spiking Solution	2500	20	50

TCLP matrix Spike Standard (5-component subset)

STOCK STANDARD	CONC (ug/mL)	microliters of stock to final volume of 1.0mL	STD CONC. ug/mL
TCLP Spiking Solution	2000	16	125

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS - EXAMPLES

The following calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	TCL-1 *	TCL-2 *	TCL-3 *	TCL-4 *	TCL-5 *	TCL-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	8260-1 *	8260-2 *	8260-3 *	8260-4 *	8260-5 *	8260-6 *
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 5.0mL of reagent water or to 5.0g of blank sand.

CONCENTRATIONS OF THE CALIBRATION STANDARDS-5.0mL OR 5.0g

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
TCL-1,8260-1	5ug/l-kg	25ug/l-kg
TCL-2,8260-2	10ug/l-kg	50ug/l-kg
TCL-3,8260-3	25ug/l-kg	125ug/l-kg
TCL-4,8260-4	50ug/l-kg	250ug/l-kg
TCL-5,8260-5	100ug/l-kg	500ug/l-kg
TCL-6,8260-6	200ug/l-kg	1000ug/l-kg

Appendix A

VOLATILES BY GC/MS CALIBRATION STANDARDS-25mL Purge Volume-EXAMPLES

These calibration standards are prepared to define the working range of the EPA 8260 analysis for the target compound list (TCL) and the extended list of compounds generally associated with EPA 8260. The standards are based on a volume of 25mL to achieve lower quantitation limits for the target compounds. The lowest level standard is at the reporting limit and the other standards define the working range. Samples with target analytes above the concentration of the highest calibration standard must be diluted and reanalyzed.

TARGET COMPOUND LIST

Working Level standards	Conc (ug/mL)	25TCL -1*	25TCL-2*	25TCL-3*	25TCL-4*	25TCL-5*	25TCL-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

8260 EXTENDED LIST (TCL+ADDITIONAL COMPOUNDS)

Working Level standards	Conc (ug/mL)	258260-1*	258260 -2*	258260-3*	258260-4*	258260-5*	258260-6*
TCL WS-1	25/125	1.0	2.0	5.0	10.0	20.	40
TCL WS-2	125	1.0	2.0	5.0	10	20	40
8260 WS-3	25	1.0	2.0	5.0	10	20	40
TCL GASES	25	1.0	2.0	5.0	10	20	40
TCL ISTD	50	5.0	5.0	5.0	5.0	5.0	5.0

*uL of the working standard added to 25mL of reagent water.

CONCENTRATIONS OF THE CALIBRATION STANDARDS

Cal Std	all targets except ketones, 2-CEVE	ketones, 2-CEVE
25TCL-1,25-8260-1	1.0ug/l	5.0ug/l
25TCL-2,25-8260-2	2.0ug/l	10ug/l
25TCL-3,25-8260-3	5.0ug/l	25ug/l
25TCL-4,25-8260-4	10ug/l	50ug/l
25TCL-5,25-8260-5	20ug/l	100ug/l
25TCL-6,25-8260-6	40ug/l	200ug/l

Appendix B
8260 SOP SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage*	Container	Hold Time
Aqueous	None; 4C	40mL no headspace	7 days
	HCl pH<2; 4C	40mL-no headspace	14 days
Soil/solid(low level)	Iced at collection; 5mL sodium bisulfate added upon arrival in lab; store at 4C	5-g Encore Sampler	14 days
Soil/solid(low level) -high carbonates	Iced at collection; 5mL water added upon arrival in lab; store at –10C	5-g Encore Sampler	14 days
Soil/solid(high level)	None; 4C	Glass 125mL	14 days
TCLP	HCl pH<2; 4C	Tedlar bag or syringe	14 days

*storage temperature is 4C with a control criteria of less than 6C with no frozen samples

ANALYSIS SEQUENCE

INITIAL CALIBRATION	CONTINUING CALIBRATION
4-BFB 50ng on column Clock starts at injection	4-BFB 50ng on column Clock starts at injection
Calibration standards- minimum of five cal levels	Mid point calibration verification (50ug/L or 50ug/kg)) RL Standard-low point on cal curve (if necessary)
Method blank	Method blank
Samples analyzed until the 12-hour clock expires	Samples analyzed until 12-hour clock expires

See SL SOP AN02, Section 3.1.3, for the batch/clock options for LCS and MS/MSD.

Recommended Internal Standards:
1,2-dichloroethane-d4; 1,4-difluorobenzene; chlorobenzene-d5; 1,4-dichlorobenzene-d4

Surrogates/System Monitoring Compounds:
dibromofluoromethane; toluene-d8; 4-bromofluorobenzene

LCS/MS: CQAP Subset:
1,1-dichloroethene; benzene; trichloroethene; toluene; chlorobenzene

Appendix B
8260 SOP SUMMARY

VOLATILE ORGANIC GC/MS TUNING AND MASS CALIBRATION BROMOFLUOROBENZENE (BFB)	
m/e	**Abundance Criteria**
50	8.0-40.0% of mass 95
75	30.0-66.0% of mass 95
95	Base peak, 100% relative abundance
96	5.0-9.0% of mass 95
173	< 2.0% of mass 174
174	50-120%% of mass 95
175	4.0-9.0% of mass 174
176	93.0-101.0% of mass 174
177	5.0-9.0% of mass 176

(1) *8260 criteria taken from CLP OLMO4.0 (January 1998)

CALIBRATION ACCEPTANCE CRITERIA

Calibration Check Compounds - CCC
Vinyl chloride, 1,1-dichloroethene, chloroform, 1,2-dichloropropane, toluene, ethylbenzene

Initial Calibration	**Continuing Calibration**
Less than or equal to 30% RSD	Less than or equal to 20% difference or drift from initial calibration

System Performance Check Compounds-SPCC

SPCC	Minimum RRF
Chloromethane	0.10
1,1-Dichloroethane	0.10
Chlorobenzene	0.30
Bromoform	>0.10
1,1,2,2-Tetrachloroethane	0.30 (0.10 for 25mL purge volume)

See Sections 10.3 and 10.4 for ICAL and CCV linearity checks and criteria.

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
MS Tune Check - 50ng 4-BFB	Before initial and continuing calibration standards - every 12 hours	Mass abundances within method acceptance criteria	-Evaluate chromatogram and spectrum - Reanalyze - Retune MS and reanalyze - Remake standard and reanalyze - Perform instrument maintenance and reanalyze
Initial Calibration – minimum five point curve with lowest point at or below the Reporting Limit (RL)	Initially; after major instrument maintenance; whenever continuing calibration check fails. Prior to analysis of method blank and samples	Method criteria for CCC/SPCC (see -Calibration Acceptance Criteria – Table presented earlier in this document)	- Evaluate chromatograms, spectra, and integrations - Reanalyze standard(s) - Remake and reanalyze standard(s) - Perform instrument maintenance and recalibrate
Continuing Calibration check - midpoint standard	Every 12 hours before analysis of method blank and samples	Method criteria for CCC/SPCC (see Calibration Acceptance Criteria - Table presented earlier in this document)	- Evaluate chromatogram, spectra, integrations - Reanalyze standard - Remake and reanalyze standard - Recalibrate - Perform instrument maintenance and recalibrate
Method Blank	Every 12 hours (per clock) before sample analyses	All reported targets <RL	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Lab Control Sample (LCS) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Matrix Spike/Matrix Spike Duplicate (MS/MSD) -subset of target compounds unless full target spike specified by client	Each batch	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Surrogates	All samples, blanks, LCS, MS	STL-SL CQAP Section 5	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL-SL SOP AN02 and Table 13.1 in CQAP -Perform instrument or column maintenance, recalibrate, and reanalyze
Internal Standard Area	Evaluate all standards and samples	-Areas in continuing calibration verification must be 50% to +200% of previous initial calibration sequence -Retention time of internal standard must be +/-30 seconds from internal standard in initial calibration -Areas in samples should be evaluated for gross error . Consult supervisor.	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze

Appendix B

QC Check	Frequency	Acceptance Criteria	Corrective Action
Reporting Limit Standard -1x to 2x the RL	(Optional) Daily. Required for Florida DEP	Detected with reasonable response	-Evaluate chromatogram, spectra, and integrations -Reanalyze -Remake standard and reanalyze -Retune and recalibrate -Perform instrument maintenance and recalibrate
Initial Demonstration of Capability	Per analyst	Method criteria	-Reanalyze targets that do not meet criteria
Method Detection Limit (MDL)	See STL-SL SOP CA90	See STL-SL SOP CA90	-Reanalyze and re-evaluate

Appendix C
EXAMPLE QUANTITATION REPORT

-quantitation ions
-internal standard and target compound association

SEVERN TRENT STL

PREPARATION, SCREENING, AND STORAGE OF VOLATILES SAMPLES

Approved by:

R. Wayne Robbins — R. Wayne Robbins   30 Aug 2002
Date

Title: Technical Manager

STL X Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

This SOP describes the procedures that are used to prepare and screen samples for volatile organic compounds (VOC) in water and soils by GC and GC/MS.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Aqueous samples are checked for sample integrity and pH and are screened by GC/FID. The pH of the sample is documented at log-in. If the sample integrity or hold time has been compromised, the project manager must be notified.

2.2 Soils are routinely collected in Encore devices. Three Encore devices and a bulk container are routinely received for each sample. The bulk sample is used to determine the type of preservation required, the percent solids, and to perform the screening analysis. Samples collected in Encore devices are transferred to vials and preserved within 48 hours of collection. Two of the vials are routinely used for low-level analysis and the third preserved in methanol for high level analysis, if required. If the sample integrity or hold time has been compromised, the project manager must be notified.

2.3 Definitions

VOC – volatile organic compound(s)
VOA – volatile organic analytes (analysis)

2.4 This method is based on the guidance in SW-846 Methods 5021, 5030, 5035.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put yourself or others in a potentially hazardous situation.

3.2 Each chemical compound should be treated as a potential health hazard. Exposure to these chemicals must be reduced to the lowest level possible. Lab coats, gloves, eye protection, or other equipment should be used. Standards and highly contaminated samples should be handled in a hood.

3.3 Material Safety Data Sheets (MSDS) are available to the analyst. These sheets specify the type of hazard that each chemical poses and the procedures that are used to safely handle these materials.

4.0 INTERFERENCES

4.1 VOCs commonly used in the laboratory are potential sources of contamination. Methylene chloride, acetone, Freon-113, MEK, hexane, toluene, and isopropanol are used in the laboratory and tend to present the most problems.

4.2 The volatiles lab must be kept as free from contamination as possible. Highly contaminated samples must be segregated from routine samples. Contact with sections of the laboratory where solvents are used should be minimized. Refrigerator blanks should be prepared, stored, and analyzed to evaluate the sample storage areas for possible contamination. Guidance is provided in SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

5.0 SAMPLE COLLECTION, HANDLING, AND PRESERVATION

5.1 Liquids: Aqueous samples are routinely collected with no headspace in 40mL vials equipped with Teflon-lined caps. The samples are acidified at the time of collection with about 0.30mL of concentrated HCl per 40mL of sample. The acid prevents the biological degradation of the aromatic compounds and prevents the dehydrohalogenation of some of the chlorinated alkanes. The sample must be iced at the time of collection and refrigerated at 4C (less than 6C with no frozen samples) in the lab until analysis.

The holding time for samples preserved with HCl is 14 days for all target compounds. The holding time for unpreserved samples is 7 days.

5.2 Soils: Soils are routinely collected in triplicate in Encore samplers. A "bulk" sample is also routinely collected in a 125-mL jar fitted with a Teflon-lined cap. The bulk sample is used for determining the percent solids and can be used for the methanol extraction if the concentration of the sample collected in the Encore exceeds the working range of the analytical system.

Soils collected in Encore samplers must be analyzed within 48 hours of collection or must be preserved using sodium bisulfate solution within 48 hours of collection. If the sample contains high levels of carbonates, the sample is preserved with water and frozen until the time of analysis. The procedure for preparing soil samples is given in Section 9.2.

The hold time for the preserved sample is 14 days from the date of collection. The hold time for frozen samples is 14 days from the date of collection.

5.3 Field Preserved Soils
Soil samples may be collected in pre-weighed vials containing either sodium bisulfate or methanol preservative. The vials with preservative are routinely weighed in the lab, the tare weight is recorded, and the containers sent to the field. The samples are collected and returned to the lab where the container is weighed and the weight of the sample determined by the difference. The hold time for field preserved samples is 14 days from the date of collection.

5.4 High level soil and waste samples are collected in glass containers (usually 125-mL clear glass) equipped with Teflon-lined caps. Soil samples may also be submitted as core samples contained in Encore samplers, in metal or plastic "tubes", or in 40-mL VOA vials. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples). The holding time for soil and waste samples subjected to methanol extraction is 14 days from date of collection. Extraction and analysis must be completed within 14 days of collection.

5.5 TCLP leachate samples are collected with no headspace in Tedlar bags or syringes. The leachate samples are acidified after the leaching procedure with about 0.10mL of concentrated HCl per 40mL of sample and stored at 4C (less than 6C with no frozen samples) from the time leaching is completed until the analysis. The acidified leachate sample must be analyzed within 14 days of the leaching procedure. If the sample is not acidified, the leachate must be analyzed within 7 days of the leaching procedure.

NOTE: Samples that are suspected of having very high concentrations of VOC should be segregated from the "routine" samples and stored in a manner that will minimize sample and laboratory contamination. See SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples* for guidance. If possible, keep the field QC in the same storage refrigerator as the samples.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph with flame ionization detector (FID)

6.2 Headspace device: Tekmar 7000 or equivalent

6.3 Data System compatible with the analytical system

6.4 Microsyringes: 100uL

6.5 Gastight syringe: 5mL, 25mL

6.6 Volumetric flasks: various sizes

6.7 Recommended Column: J&W DB-624, 30m x 0.53mmID x 3.0um or equivalent

6.8 Headspace vials with crimp-top septum caps

6.9 40-mL VOA vial with methanol preservative: weigh and record vial before sending to the field

6.10 40-mL VOA vial with sodium sulfate preservative: weigh and record vial before sending to the field

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability.*

7.1 Reagent water - free of volatile contaminants (obtained by purging with inert gas or carbon filtration)

7.2 Methanol - Purge and Trap grade

7.3 Sodium bisulfate - reagent grade. This salt is hydroscopic and should be stored in a dessicator.

7.4 Sodium bisulfate soil preservation solution - Slowly add, while stirring, 200g of sodium bisulfate to a 1.0-L volumetric flask containing about 700mL of reagent water. After the salt has dissolved, dilute to volume with reagent water, transfer to a storage container, and store the solution in an area free from VOC - especially water-soluble solvents such as acetone. The reagent should be tested prior to use by the analysis of a blank containing 5mL of the solution. The reagent is acceptable if it meets the same criteria as a method blank.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions purchased from vendors or from stock standards prepared from neat materials. Certificates of analysis or purity must be received with all stock solutions or neat compounds. All preparation steps must be in accordance with SOP AN41: *Standard Material Traceability.*

Prepare calibration standards containing the following compounds at 50, 100, 200, 400, 800, and 1600ug/L in reagent water: methlyene chloride, 1,1-dichloroethene, cis-1,2-dichoroethene, chloroform, benzene, trichloroethene, toluene, tetrachloroethene, ethylbenzene, m/p-xylene, o-xylene, 1,3-dichlorobenzene, 1,4-dichlorobenzene, and 1,2-dichlorobenzene.

Transfer 4mL of the calibration standard to a labeled headspace vial and add 1mL of reagent water. Analyze according to Section 10.

9.0 SAMPLE PREPARATION

Composite samples can be prepared using the guidance in SOP AN70: *Compositing and Homogenization of Field Samples and Segregation of Low and High Concentration Volatile and Semivolatile Samples.*

9.1 Preparation of Aqueous Samples

Aqueous samples are analyzed directly by purge and trap GC and GC/MS. No sample preparation is necessary except to homogenize the sample prior to subsampling. The pH of liquid samples is checked and recorded prior to analysis and recorded on the appropriate log.

9.1.1 Samples are logged into the Volatiles' Liquid Logbook. Three vials are routinely received and the vials are designated A, B, and C. If more than three vials are received, then letter accordingly. Use the last vial for the screening and pH determination.

9.1.2 Check each sample vial at the time of receipt for the presence of "bubbles". If the bubbles are less than 3mm in diameter, the vial is acceptable. If all vials contain bubbles greater than 3mm, notify the department supervisor or project manager that there are no acceptable vials for analysis.

9.1.3 Use the "C" vial (or last vial) for screening and pH check. (If a vial contains air bubbles, then sacrifice this vial for screening and pH determination, since the sample is already compromised. Save acceptable vials for analyis.)

Determine the pH of the sample using narrow range pH paper and record in the Volatiles' Liquid Logbook.

If the sample pH is greater than 2, fill out a 7-Day Hold Sheet and notify the department supervisor. All samples with pH greater than 2 must be analyzed within 7 days of collection. All samples with pH less than 2 must be analyzed within 14 days of collection.

Transfer 4mL from the C vial to a labeled headspace vial and add 1mL of reagent water. Analyze this screening vial according to Section 10. Evaluate the results according to Section 11.

9.1.4 Transfer the A and B vials to the storage racks. Store the screening C vial separately from the A and B vials.

9.2 Preparation of Soil Samples (5035)

The preparation of soil samples must be performed within 48 hours of collection. Three Encore devices and one bulk container are routinely received for each sample. Two of the Encores are prepared for low level analysis, and one is extracted in methanol. The bulk container is used for determining the type of preservation for the low level samples and, if required, for screening. The Encores are labeled as the A, B, and C samples.

NOTE: If soil samples are received in 25-g Encore devices, contact the supervisor immediately to confirm the preparation steps. The procedures given below are to be used as the default.

9.2.1 Low Level Preparation (A and B Vials)

9.2.1.1 Carbonate Test

Transfer a small aliquot (~0.5g) of sample from the bulk container to a 20-mL scintillation vial.

Add approximately 5mL of the sodium bisulfate preservation solution.

If the sample fizzes (effervesces), preserve with volatile-free water and place in a freezer at –10C. If no fizzing is noted, preserve with 5mL of the soil preservation solution (sodium bisulfate) and store at 4C in the soil storage refrigerator.

9.2.1.2 Add a stir bar to a 40-mL vial. Attach the bar code label and ID label to the 40-mL vial. Write the sample ID and vial designation (A or B) on the ID label. Place the vial on the balance and tare the vial and stir bar weight by pressing the autotare button.

9.2.1.3 Transfer the sample from the Encore device to the labeled, tared vial and record the weight of the sample to the nearest 0.01g in the Volatile Soil Sample logbook.

NOTE: If the sample is received in a 25-g Encore device, transfer two 5-g (5.0-5.5g) aliquots from the device to the tared vials (A and B). Transfer a third 5-g aliquot to the C-vial for methanol preservation (Section 9.2.2). A plastic syringe may be used to remove an aliquot of the sample from the 25-g sampler. On average, a 3mL plug of soil will be approximately 5g.

If the sample fizzed during the carbonate test (9.2.1.1), add 5mL of reagent water and freeze at –10C. If the sample did not fizz, add 5mL of the soil preservation solution and store the sample at 4C until the time of analysis. The preserved samples must be analyzed within 14 days of collection.

Place samples from the same log number with the same preservation in a plastic bag and seal. Write the log number and type of preservation on the outside of the bag. For example, put all of the sodium bisulfate preserved samples together, all of the water preserved samples together, and all of the methanol preserved samples together. Do not put samples from different log numbers in the same bag.

9.2.2 Methanol Preservation (C Vial)
A methanol extraction is prepared from the third Encore device or from the bulk container when an Encore is unavailable. Carry out the preparation quickly to minimize the loss of volatiles.

9.2.2.1 Attach the bar code label and ID label to a 40-mL vial. Write the sample ID and vial designation (C) on the ID label. Place the vial on the balance and tare the vial and stir bar weight by pressing the autotare button.

9.2.2.2 Transfer the sample from the Encore to a 40-mL VOA vial.

NOTE: If the sample is received in a 25-g Encore device, transfer 5-g aliquot to the C-vial for methanol preservation after taking the two 5-g aliquots for low level analysis (Section 9.2.1.2).

Add 5mL of methanol and shake vigorously for approximately 10 seconds.

Put in bag and seal. Samples preserved in methanol from the same log number may be put in same bag. Do not put samples from different log numbers in the same bag.

Store in refrigerator at 4C.

9.2.2.3 Transfer 100uL (0.1mL) of the methanol extract (Vial C) to 5mL of reagent water contained in a labeled headspace vial. Analyze this screening vial according to Section 10. Evaluate the results according to Section 11.

9.3 Pre-Weighed Vials with Methanol or Sodium Bisulfate Preservative

9.3.1 Pre-sampling

9.3.1.1 Select number of vials for sampling. Attach label if not already attached but do not obscure the vial identification number. Inspect each vial to ensure that there is preservative at the correct volume, that the cap is secure, and that there is no extraneous material or moisture adhering to the outside of the vial.

9.3.1.2 Weigh the vial and record the weight and vial identification in the appropriate logbook. Record the weight to the nearest 0.01g.

9.3.1.3 Pack the vials and transfer to the shipping and receiving department. Include at least one trip blank with each set of vials.

9.3.2 Post-sampling

9.3.2.1 Remove vials from storage and allow them to come to room temperature.

9.3.2.2 Wipe off any extraneous moisture or material adhering to the outside of the vial.

9.3.2.3 Weigh and record the weight of the vial, sample, and preservative to the nearest 0.01g. Calculate the weight of the sample as:

$$W_{sample}(g) = W_2 - W_1$$

where:
W_2 = weight of sample, vial, and preservative (g)
W_1 = weight of vial and preservative (g)

9.3.2.4 Shake the vial for approximately two minutes.

9.3.2.5 Screening
Remove 100uL (o.10mL) of the extract through the septum and transfer to 5.0mL of water. Screen sample as in Section 10.

9.3.2.6 Store the remaining extract at 4C until the time of analysis.

10.0 PROCEDURE

10.1 Screening Instrument Conditions

The instrument parameters are provided as examples. The actual operating parameters and conditions must be documented in the appropriate log.

Gas Chromatograph Program for DB-624 column:

Initial temperature:	50 C for 2.0 minutes
Temperature Ramp:	16 C per minute
Final Temperature:	200 C for 1.0 minute

Set column flow to provide adequate separation of analytes. Set makeup and detector gases according to manufacturer's instructions.

Tekmar 7000 Headspace Analyzer Parameters:

Temperature to heat vials:	85C
Equilibration time:	10 minutes
Mixing time:	1 minute
Volume of headspace analyzed:	1mL
Heated line temperatures:	100C

10.2 Screening Calibration

Analyze the six calibration standards outlined in Section 8.0. Prepare a calibration curve in accordance with SOP AN67: *Evaluation of Calibration Curves*. An external calibration curve is prepared with nanograms (ng) of compound plotted on the x-axis.

ICAL Criterion: Use professional judgement
CCV Criterion: +/-50% of true value

10.3 Screening Analysis

An ICAL should be analyzed initially and when the percent difference of the CCV exceeds 50%. The CCV and a method blank should be analyzed daily prior to sample screening.

10.3.1 Liquid Samples

Transfer the screening vial from Section 9.1.3 to the autosampler and analyze. Evaluate data according to Section 11.

10.3.2 Soil Samples

Transfer the screening vial from Section 9.2.2.3 to the autosampler and analyze. Evaluate data according to Section 11.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Identify the compounds based on the retention time and compare the nanograms (ng) of compound to the upper level of the liquid or soil calibration curve.

11.2 Liquids: Calculate the dilution (as dilution factor, DF) to run on the instrument as follows:

$$DF = \frac{ng(screen)}{ng(cal)}$$

where:
ng(screen) = nanograms of compound from screening run
ng(cal) = nanograms of upper level of calibration curve

If the ratio is<=1, run at DF=1. If the ratio is >1, run at next highest whole number DF. For example, if ratio is 1.5, run at DF=2.

11.3 Soils: Calculate the dilution (as dilution factor, DF) to run on the instrument as follows:

$$DF = \frac{ng(screen)}{ng(cal)} \otimes 50$$

where:
ng(screen) = nanograms of compound from screening run
ng(cal) = nanograms of upper level of calibration curve

If the ratio is<=5, run at DF=1. If the ratio is >5, run methanol extraction.

NOTE: the factor of 50 is the ratio of the low level soil weight (5g) divided by the weight of sample (0.1g) analyzed in the screening analysis.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

There are no formal QC or QA requirements for this SOP since the results are used to estimate the dilution used for the definitive analysis of the samples. The analyst must use good professional judgement in evaluating the data. A method blank should be analyzed each day screening takes place.

13.0 TROUBLE-SHOOTING AND PREVENTIVE MAINTENANCE

See instrument manufacturer's manual and SOP AN53: *Maintenance Procedures for Laboratory Instruments* for preventive maintenance and troubleshooting guidance.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Excess samples, extracts, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management.*

15.0 REFERENCES

Test Methods for Evaluating Solid Wastes, Third Edition, SW-846.including Update III U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC.

SEVERN TRENT STL

MERCURY PREPARATION AND ANALYSIS

(Methods: EPA 7470A, 7471A, and 245.1)

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Date

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STL Savannah

Safety Approval:

Ernest R. Watts — 02/03/04
Date

Title: EHSC
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1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedure to determine the concentration of mercury by cold vapor atomic absorption spectrophotometry (CVAA). This method contains the manual preparation and the analytical procedures for determination of mercury in aqueous liquids (water), surface and groundwaters, soils, sediments, sludges, wastes and leachates (EP or TCLP) after digestion.

1.2 The reporting limit (RL), method detection limit (MDL), and the accuracy and precision criteria are listed in the current revision of the *Laboratory Quality Manual* (LQM) prepared by and for STL Savannah.

2.0 SUMMARY OF THE METHOD AND DEFINTIONS

2.1 This method is based on the absorption of characteristic radiation at 253.7nm by mercury vapor. After digestion, to convert all forms of mercury to the same oxidation state, the mercury ions are reduced to mercury by the addition of stannous chloride and aerated from solution after passing through a mixing coil. The mixture passes through a gas/liquid separator and through a drying tube. The vapor is passed through a flow cell positioned in the light path of an atomic absorption spectrophotometer. Mercury concentration is measured as a function of absorbance

2.2 Definitions – Refer to SOP AN99: *Definitions, Terms, and Acronyms* for a complete listing of applicable definitions.

CVAA - cold vapor atomic absorption
TCLP – toxicity characteristic leaching procedure
EP Tox - extraction procedure toxicity
Analytical Spike - addition of a known concentration of analyte to an aliquot of sample after the preparation steps have been performed; also called a post digestion spike
RL - reporting limit, the lowest calibration standard or the sample equivalent of the lowest calibration standard; published in LQM or project-specific quality assurance plan (QAPP); sometimes referred to as the "practical quantitation limit" (PQL).
MDL - method detection limit, the concentration that can be reported with 99% confidence that the result is greater than zero; published in LQM

2.3 This method is based on the guidance provided in SW-846 methods 7000A, 7470A, 7471A, and EPA method 245.1 (Drinking Water version).

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, the Waste Management SOP, and this document.

3.1 Specific Safety Concerns or Requirements

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers, and staining of the skin to a yellow or yellow-brown color. These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Sulfuric acid is a strong oxidizer and is a corrosive. It will react violently when combined with organic compounds, possibly producing fire. Inhalation can cause irritation of the nose, throat, mucus membranes, and upper respiratory tract. Contact with the eyes can cause blurred vision, redness, pain, and even blindness.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

The making of aqua regia can produce toxic fumes and heat This procedure must be performed under a working fume hood.

The exhaust of the mercury analyzer must be vented or trapped so that mercury vapors do not enter the laboratory.

3 2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: **This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison	1Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose and throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue bums. Can cause blindness.
Nitric Acid	Corrosive Oxidizer Poison	2ppm-TWA 4ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe bums and permanent eye damage.
Hydrochloric Acid	Corrosive Poison	5ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin bums. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Potassium Permanganate	Oxidizer	5Mg/M3 for Mn Compounds	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Dry crystals and concentrated solutions are caustic causing redness, pain, severe burns, brown stains in the contact area and possible hardening of outer skin layer. Diluted solutions are only mildly irritating to the skin. Eye contact with crystals (dusts) and concentrated solutions causes severe irritation, redness, and blurred vision and can cause severe damage, possibly permanent.
Potassium Persulfate	Oxidizer	None	Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath. Causes irritation to skin and eyes. Symptoms include redness, itching, and pain. May cause dermatitis, bums, and moderate skin necrosis.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 INTERFERENCES

4.1 Potassium permanganate is added to eliminate the possibility of interference from sulfide and certain organic compounds.

4.2 Chlorine is known to interfere with this analysis. Addition of extra potassium permanganate may be needed during the digestion of samples containing chloride. Also, the samples are not capped tightly during digestion so that excess chlorine can escape.

4.3 Contamination of the sample can occur when the preparation glassware and/or reagents contain mercury. Reagent blanks (method blanks) must be analyzed as a check on contamination due to sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

5.1 Aqueous samples and TCLP/EP-TOX Leachate

5.1.1 Liquid samples are collected in 250-mL plastic or glass containers. The samples are preserved with HNO_3 to a pH<2. Samples must be digested and analyzed within 28 days of collection.

5.1.2 Samples for dissolved mercury should be filtered in the field before acid is added to the sample. If the sample is to be filtered in the lab, no preservative is added to the sample until the sample is filtered. The sample is stored at 4°C (less than 6°C, but not frozen) until filtration and preservation.

5.2 Soil/Sediment/Waste Samples

5.2.1 Soil and sediment samples are collected in 250-mL or 500-mL plastic or glass containers. The samples are iced at the time of collection and stored at 4°C (less than 6°C but not frozen) until the time of digestion and analysis. Samples must be digested and analyzed within 28 days of collection.

6.0 APPARATUS AND MATERIALS

6.1 Leeman Hydra AA or other suitable automated mercury analyzer with data system and printer

6.2 Nitrogen or argon gas supply and appropriate fittings

6.3 Pump tubing of appropriate sizes for use on the Hydra AA

6.4 Volumetric glassware for making standards and reagents

6.5 Test tubes of the two sizes to fit the Hydra AA autosampler

6.6 Water bath or heating block capable of maintaining a temperature of 95 ± 5°C

6.7 Digestion glassware

7.0 REAGENTS

All reagents must be tracked in accordance with SOP AN44: *Reagent Traceability*.

7.1 Reagent water-lab generated deionized water, ASTM Type I or Type II. The conductivity is monitored in accordance with SOP AN35: *Conductivity Checks for Laboratory Deionized Water*.

7.2 Nitric Acid (HNO_3), concentrated-reagent grade

7.3 Hydrochloric Acid (HCl), concentrated-reagent grade

7.4 Aqua regia: Prepare immediately before use by carefully adding three volumes of concentrated HCl to one volume of concentrated HNO_3.

7.5 Potassium permanganate, mercury-free, 5% solution (w/v): Dissolve 50g of $KMnO_4$ in 1000mL of DI water.

7.6 Sodium chloride-hydoxylamine sulfate solution: Dissolve 120g NaCl and 120g hydroxylamine sulfate in DI water in a 1-L volumetric flask and dilute to volume.

7.7 Potassium persulfate, 5% solution (w/v): Dissolve 50g potassium persulfate in 1000mL DI water.

7.8 Rinse Water, 5% HCl-1%HNO3 - to a clean 2-L bottle add 1-L of reagent water. Carefully add 100mL of concentrated hydrochloric acid. Carefully add 20mL of concentrated nitric acid. Dilute to a final volume of 2L. Other volumes may be utilized providing the reagent proportions remain the same.

7.9 Stannous chloride ($SnCl_2.2H_2O$) - reagent grade, suitable for mercury determination

7.10 Stannous chloride ($SnCl_2.2H_2O$) solution - to a clean 2-L volumetric flask add 100g of stannous chloride. Add approximately 400mL of reagent water Carefully add 500mL of concentrated hydrochloric acid. Add a stirring bar and stir on a stir plate until the stannous chloride is dissolved Remove the stirring bar and dilute to volume with reagent water

7.11 Magnesium perchlorate ($Mg(ClO_4)_2$) - used as a drying agent in the drying tube. The magnesium perchlorate should be as coarse as possible.

7.12 Sulfuric Acid (H_2SO_4), concentrated reagent grade

8.0 STANDARDS

All standards must be tracked in accordance with SOP AN41: *Standard Material Traceability*.

8.1 Commercial stock standard, 1000mg/L.

8.2 Independent stock standard, 1000mg/L.

8.3 Calibration standards

8.3.1 Mercury calibration intermediate stock standard, 10mg/L: Add 1mL of the commercial stock standard, 1000mg/L, and 2.5mL of nitric acid to about 50mL of DI water in a 100-mL volumetric flask and dilute to volume.

8.3.2 Mercury intermediate working standard, 500µg/L: Add 5mL of the 10mg/L intermediate stock standard and 2.5mL of nitric acid to about 50mL of DI water in a 100-mL volumetric flask and dilute to volume.

8.3.3 Mercury Calibration Standards: Transfer 0.0, 0.02, 0.04, 0.1, 0.3, and 0.5mL portions of the intermediate working standards to a series of 125mL glass bottles. Add DI water from a graduated cylinder to each bottle to make a final volume of 50mL. This results in working standard concentrations of 0.0, 0.2, 0.4, 1.0, 3.0, and 5.0µg/L mercury. Mix well and add 2.5mL of concentrated H_2SO_4, 1.25mL of concentrated HNO_3, and 7.5mL of $KMnO_4$ solution and let stand at least 15min. Add 4mL of potassium persulfate and heat for 2 hours in a water bath at 95°C. Cool and add 3mL of sodium chloride-hydroxylamine sulfate solution to reduce the excess permanganate. The standards are ready for analysis. Larger volumes of standards may be digested as needed as long as reagent ratios are kept the same.

8.4 Calibration verification standards - Initial (ICV) and Continuing (CCV):

8.4.1 Verification intermediate stock, 5.0mg/L: Add 0.5mL of the Independent stock standard, 1000mg/L, and 2.5mL of nitric acid to about 50mL of DI water in a 100-mL volumetric flask and dilute to volume.

8.4.2 Verification Working Stock, 250µg/L: Add 5mL of the verification intermediate stock, 5.0mg/L, and 2.5mL of nitric acid to about 50mL of DI water in a 100-mL volumetric flask and dilute to volume.

8.4.3 Initial Calibration Verification (ICV) Standard, 3.0µg/L: Add 0.60mL of the verification working stock, 250µg/L, to a 125-mL glass bottle and add enough reagent water from a graduated cylinder to make a final volume of 50mL. The ICV is now ready to be digested. Other final volumes may be used as long as the reagent ratios are kept the same.

8.4.4 Continuing Calibration Verification (CCV) Standard, 2.5µg/L: Add 0.50mL of the verification working stock, 250µg/L, to a 125-mL glass bottle and add enough reagent water from a graduated cylinder to make a final volume of 50mL. The CCV is now ready to be digested. Other final volumes may be used as long as the reagent ratios are kept the same

8.5 QC Standards

8.5.1 Matrix Spike/Matrix Spike Duplicate (MS/MSD) Working Stock, 100µg/L: Add 2mL of the verification intermediate stock, 5.0mg/L, and 2.5mL of nitric acid to about 50mL of DI water in a 100-mL volumetric flask and dilute to volume.

8.5.2 MS/MSD, 1.0µg/L (0.05 mg/kg): To two portions of a selected sample (50mL for aqueous or 1.0-1.2g of a solid sample) add 0.5mL of the MS/MSD working standard. The MS/MSD is now ready for digestion. Where sufficient sample is available, at least 1 set of MS/MSDs should be prepared and analyzed with each batch of 20 samples or less.

8.5.3 Analytical Spike Stock Standard, 73.26µg/L: Add 2mL of the verification intermediate stock, 5.0 mg/L, and 2.5mL of nitric acid to about 50mL of DI water and dilute to 136.5mL final volume

8.5.4 Analytical Spike, 1µg/L: To a 10mL portion of digested sample, add 0.1mL of the Analytical Spike Stock Standard. One analytical spike is required per batch of twenty samples or less.

8.5.5 Lab Control Standard for Water Samples (LCSW) - 2.5µg/L: Add 0.50mL of the verification working stock, 250µg/L, to a 125mL glass bottle and add enough reagent water from a graduated cylinder to make a final volume of 50mL. The LCSW must be digested/prepared in the same manner as the samples. At least 1 LCSW must be digested with each batch of 20 samples or less.

8.5.6 Lab Control Standard for Soils Samples (LCSS): Weigh an appropriate weight of a certified solid reference standard into the digestion bottle, an example would be 0.10g of the NIST 2709 San Joquin Soil The lab control standard must be digested/prepared in the same manner as the samples.

9.0 SAMPLE PREPARATION

This section describes the manual digestion procedures for aqueous, soils/wastes, and biological matrices.

9.1 Liquid samples

9.1.1 Mix the sample thoroughly and add 50mL of sample or an aliquot of sample diluted to 50mL to a 125-mL glass bottle.

9.1.2 Add 1.25mL HNO_3, 2.5mL H_2SO_4, and 7.5mL of $KMnO_4$ solution to each sample. Shake well after each addition. Be sure the purple color of $KMnO_4$ persists for at least 15min If not, add up to three times more $KMnO_4$ solution. Equal quantities of $KMNO_4$ must be added to the LCS and MB.

9.1.3 Add 4mL of potassium persulfate to each sample, shake well, and place the samples in a water bath or block digestion apparatus at 95 ± 5°C for 2 hours.

9.1.4 Remove and allow the samples to cool. Add 3mL of hydroxylamine sulfate solution to each bottle to neutralize excess $KMnO_4$ Follow the analysis procedure below (Section 10)

9.1.5 If a different final volume is obtained (due to additional $KMNO_4$ or other reason) a dilution factor must be obtained in order to correct the final result.

9.2 Soil/Solid Samples

9.2.1 Homogenize the sample thoroughly and weigh between 1.0g and 1.2g wet weight of sample into a 125-mL glass bottle

9.2.2 Add 2.5mL DI water and 2.5mL aqua regia Heat for 2min in water bath or digestion block at 95°C.

9.2.3 Allow the samples to cool to room temperature and add 25mL DI water and 7.5mL $KMnO_4$ solution to sample. Mix and heat for 30 minutes at 95 ± 5°C.

9.2.4 Allow the samples to cool to room temperature and add 3mL sodium chloride-hydroxylamine sulfate solution to reduce excess $KMnO_4$. Add 27.5mL DI water and shake well. Follow the analysis procedure below (Section 10). If additional volume(s) of $KMNO_4$ were added, compensate for the addition(s) by adding less DI water so that the final volume will remain constant.

9.3 Fish and Crustaceans
Blanks and laboratory control standards should be treated identically. All reagents that are added to the samples should be added in the same ratios to the blanks and lab control standards. Fish are calculated on an "as is" basis.

9.3.1 Weigh between 1.0g and 1.2g of the sample and place into a 125-mL glass bottle.

9.3.2 Add 2mL H_2SO_4 and 0.5mL HNO_3 to each sample and digest in the waterbath or heating block for 30min at 80°C or until the tissue is completely dissolved.

9.3.3 After samples are cooled, add 7.5mL of $KMnO_4$ (more $KMnO_4$ may be added if required), 4mL potassium persulfate solution, 25mL DI water and put samples back into water bath for an additional 90min at 30°C.

9.3.4 Remove and cool. Add 3mL hydroxylamine sulfate solution to neutralize excess $KMnO_4$. Add 26mL DI water and shake well. If additional volume(s) of $KMNO_4$ were added, compensate for the addition(s) by added less DI water so that the final volume will remain constant.

10.0 ANALYTICAL PROCEDURE

10.1 Initial startup of the instrument

10.1.1 Before analysis begins inspect the system (pump tubes, mixing coil, gas/liquid separator) to see if any parts need to be cleaned or replaced.

10.1.2 Replace the drying tube with a freshly packed drying tube, making sure that the magnesium perchlorate is not packed too tightly. The vapors must be able to pass freely through the drying tube. Alternatively inspect the pre-made drying tube from Leeman Labs (120-00281-1) for discoloration and clean or replace as needed. Caution should be used if moisture is visible in the tubing that follows the drying tube

10.1.3 Fill the rinse tank with rinse water.

10.1.4 If the lamp is not already on and warmed up, turn on the lamp. The lamp must warm up for a minimum of 2 hours.

10.1.5 If the lamp is already on and warmed up, make sure the platens are tight and turn on the pump Allow a minimum of 20 minutes of pump time for the pump tubes to break in each day.

10.1.6 Fill the stannous chloride reagent bottle with stannous chloride solution. Switch the reagent line from rinse to the stannous chloride reagent bottle. Allow the reagent to reach the sample stream before starting an autosampler run

10.1.7 Fill the stannous chloride reagent bottle with stannous chloride solution. Switch the reagent line from rinse to the stannous chloride reagent bottle.

10.2 Autosampler setup

10 2 1 Fill the standard tubes with the appropriate standards for the protocol being followed.

10.2.2 Fill the labeled sample test tubes with the samples and calibration verification standards in the applicable order. An example order is as follows:

ICV - Initial Calibration Verification Standard
ICB - Initial Calibration Blank
Detection limit standard
9 SAMPLES
CCV - Continuing Calibration Verification Standard
CCB - Continuing Calibration Blank
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB

The preparation blank will be analyzed first The LCS will follow immediately after the preparation blank. The samples, matrix spikes, and duplicates will then follow with a maximum of 10 analyses between CCVs/CCBs. **All samples and control samples must be labeled with the corresponding batch ID.**

10.2.3 Enter the sample/QC IDs into the autosampler table giving each rack a unique name.

10.2.4 Load the rack(s) onto the autosampler.

10.3 Calibration of the mercury analyzer.

10 3.1 Call up the required protocol Open a new data folder.

10 3.2 Go to CALIBRATION, RESET, and reset the calibration for a new calibration.

10.3.3 Go to CALIBRATION, STANDARDS, and insure that calibration standards are entered at the proper concentrations.

10.3.4 Analyze the standards, beginning with standard 1 (Blank), proceeding from lowest to highest concentration.

10.3.5 When all calibration standards have been analyzed, go to CALIBRATION, LINE CALIBRATION. If calibration is within acceptable limits (correlation > 0.995) accept the linear calibration and print the calibration curve.

10.4 Sample analysis

10.4.1 Go to AUTOSAMPLER, SETUP Enter the Rack ID (s) and the cup numbers to be analyzed.

10.5 If the concentration of a sample is above the calibration range of the Hg analyzer, the sample digestate must be diluted and reanalyzed. The amount of digestate needed to prepare the desired dilution is determined from the following equation.

$$V(digest) = \frac{V(fv)}{DF}$$

where

V(digest) = volume of sample digestate used to make the dilution (mL)
V(fv) = final volume of diluted sample (mL)
DF = dilution factor

Samples should be diluted with digested blank solution

10.5.1 The dilution factor is calculated as follows:

$$DF = \frac{V(fv)}{V(digest)}$$

where

V(digest) = volume of sample digestate used to make the dilution (mL)
V(fv) = final volume of diluted sample (mL)
DF = dilution factor

10.5.2 If a sample exceeds the calibration range of the instrument by a factor of 5 or more the samples should be re-digested and reanalyzed with a smaller amount. This would be a good check for possible positive bias of the sample by incomplete digestion of organic compounds. Initial weights or volumes of <0.2g or <1.0mL should be avoided if possible so that a representative sample can be achieved If, due to the level of mercury in the samples, greater dilutions are required, consult with your supervisor for further instructions.

Carryover from high concentration samples usually affects only the next one to two samples in the sequence. The two samples following an off-scale sample that is greater than 10µg/L must be reanalyzed to verify the presence or absence of mercury and the quantitation of mercury It is the responsibility of the analyst to clearly demonstrate that all mercury results are accurate and free from carry-over contamination.

10.6 Post Digestion Spike (Analytical Spikes)
The post digestion spike is performed to verify that samples of similar matrix types are free from interferences from each batch spiked after the preparation/digestion.

10.6.1 Select at least one sample from within a batch for the post digestion spike

10.6.2 Add a known volume of a spiking solution to a known volume of sample digestate. It is suggested that the volume of spiking solution be 1% of the volume or less of the digestate to minimize the effects of volume on the post-digestion spike. The post spiking solution is prepared at a concentration that will yield a spike concentration at or near 2 times the RL when the sample digestate is spiked.

The following equation can be used to determine the volume of spiking solution required:
where

$$V1 = \frac{C2 \otimes V2}{C1}$$

C_1 = concentration of spiking solution (mg/L)
V_1 = volume of spiking solution (mL)
C_2 = desired concentration of post digestion spike (mg/L)
V_2 = volume of sample used for post-digestion spike (mL)

10.6.3 Analyze the spiked aliquot and an un-spiked aliquot.

10.6 4 Calculate the percent recovery of the post digestion spike:

$$\%REC = \frac{C_{ps} - C_s}{C_2} \otimes 100$$

where
Cps = concentration of post digestion spike (µg/L)
Cs = concentration of un-spiked sample (µg/L)
C2 = theoretical concentration of spike (µg/L) (See 10.2.5.2)

10.6.5 Evaluate the recovery using the following decision matrix. Limits for post digestion spikes are 85-115% recovery.

Result of Post Digestion Spikes	**Action**
Within 85-115% limits	None
>115% recovery	Repeat analysis Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample.
<85% recovery but >50% recovery	Analyze all associated samples by single point method of standard addition and quantify by using MSA. Or qualify all associated samples on report. If sample concentration is less than the IDL, respike (to check for a spiking error), reanalyze, and re-evaluate.
<50% recovery	Dilute digestate and repeat spike. Analyze all associated samples by single point MSA.

Note: The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high.

10.6.6 The post digestion spike and the method of standard additions must not be applied to samples analyzed at a dilution that produces a significant negative absorbance. The first point in the MSA (un-spiked sample) should be greater than or equal to zero absorbance or the magnitude of the negative response should not exceed the reporting limit. Use good judgement when evaluating data where the absorbances are negative. The digestate should be diluted and reanalyzed to determine the extract of the matrix interferences.

10.7 Single Point Method of Standard Additions

Two identical aliquots of the sample digest, Vx, are taken. One aliquot is spiked with a known concentration, Cs. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The absorbance of both aliquots are measured and the sample concentration, Cx, is calculated:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

where

S1 = absorbance of the spiked aliquot
S2 = absorbance of the un-spiked aliquot

10.8 Serial Dilution Check
A dilution is prepared and analyzed on one sample per batch to determine if matrix interferences are present.

10.8.1 Select one sample per batch for a serial dilution analysis. Analyte concentration should be ≥25 times the instrument detection limit.

10.8.2 Dilute the digestate by a factor of 5 and analyze the dilution using the same procedure used for the unspiked aliquot.

10.8.3 Compare the results of the diluted and undiluted aliquots of sample digestate.

10.8.4 If the results of the dilution are within ±10% of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than ±10% matrix interference should be suspected and the batch post-digestion spikes should be evaluated.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Aqueous and Leachate Samples

The concentration of mercury in liquid samples is routinely reported as µg/L and is calculated as follows:

$$C(sample) = C(curve) \otimes DF$$

where

C(sample) = concentration of sample (µg/L)
C(curve) = concentration from curve (µg/L)
DF = dilution factor

The RL(in μg/L) is calculated as follows:

$$RL(sample) = RL(lqm) \otimes DF$$

where

RL(sample) = reporting limit of sample (μg/L)
RL(lqm) = reporting limit from LQM (μg/L)
DF = dilution factor (The RL in the LQM assumes that DF=1)

The reporting limit (RL) may also be reported in mg/L. Results in mg/L are reported by dividing the result in μg/L by 1000.

11.2 Soil/Solid Samples

The concentration of mercury in soil and solid samples is routinely reported as mg/kg on a dry weight basis and is calculated as follows:

$$C(sample) = C(curve) \otimes \frac{F \otimes DF}{W \otimes solids} \otimes \frac{1mg}{1000ug}$$

where

C(sample) = concentration of sample (mg/kg dw)
C(curve) = concentration of digest from curve (μg/L)
F = final volume of digest (L)
W = weight of sample digested (kg)
solids = (percent solids)/100
DF = dilution factor

The reporting limit (RL) for soil/solid samples is calculated as follows:

$$RL(sample) = RL(lqm) \otimes DF \otimes \frac{1.0g}{W \otimes solids}$$

where

RL(sample) = reporting limit of sample (mg/kg dw)
RL(lqm) = reporting limit from LQM (mg/kg)
W = weight of sample digested (kg)
solids = (percent solids)/100
DF = dilution factor

RL (LQM) is based on a 1-gram sample with a percent solids of 100 (solids =1).
This equation assumes that all digests are taken to the same final volume as the standards

12.0 QUALITY CONTROL AND DATA ASSESSMENT

12.1 SOP AN02: *Analytical Batching and Evaluation of QC Data* and the SOP Summary provide guidance on evaluating QC and sample data. This guidance, including corrective actions, is summarized in Appendix A.

SOP AN02 contains the equations for the evaluation of the QC samples for accuracy and precision as well as corrective actions.

12.2 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP CA85: *Nonconformance and Corrective Action Procedures*. CA85 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures.

13.0 METHOD PERFORMANCE

The Reporting Limits (RL), the Method Detection Limits (MDL), and accuracy and precision limits associated with these methods are given in the current revision of the Laboratory Quality Manual prepared by and for STL Savannah.

13.1 Initial and Continuing Demonstration of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP *CA92: Procedure for Initial and Continuing Analyst Demonstration of Capability*.

13.2 Method Detection Limit

The method detection limit must be determined for each analyte in accordance with SOP CA90: *Procedures for the Determination of Method Detection Limit (MDL)*.

14.0 PREVENTATIVE MAINTENANCE AND TROUBLESHOOTING

14.1 Pump tubing: Inspect daily and replace as needed.

14.2 Standard Autosampler Cups: Clean daily and replace as needed.

14.3 Drying Tube: Repack daily, or more often if needed. Alternatively use the drying tube from Leeman Labs (120-00281-1) and clean and replace as needed.

14.4 Mixing Coil/Gas-Liquid Separator: Inspect weekly, clean and replace as needed.

14.5 Sample Probe: Inspect monthly, clean and replace as needed.

14.6 Mercury Lamp: Clean or replace as needed.

15.0 WASTE MANAGEMENT AND POLLUTION CONTROL

All waste will be disposed of in accordance with Federal, State and Local regulations. Follow the guidance for disposal in SOP CA70: *Waste Disposal*. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment

Excess samples, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management*.

15.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

- Excess aqueous samples – Dispose according to characterization on the sample disposal sheets. Neutralize non-hazardous samples before disposal into drain/sewer. Transfer hazardous samples (identified on disposal sheets) to the waste department for disposal.

- Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

- Acidic sample digestions – Neutralize before disposal into drain/sewer system

- Excess oil samples – Transfer to waste department for storage/disposal

16.0 REFERENCES

STL Savannah's *Laboratory Quality Manual (LQM)*, current revision

Severn Trent Laboratories' *Quality Management Plan (QMP), current revision*

Test Methods for Evaluating Solid Waste, Third Edition; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986 (SW-846 Update III).

Methods for Analysis of Water and Waste; U S. EPA Office of Research and Development: Cincinnati, OH, March 1983

17.0 TABLES, DIAGRAMS, AND VALIDATION DATA

Appendix A contains an SOP Summary which includes:

- Collection, preservation, and HT summary
- Analytical Sequence
- QC Criteria Summary

Appendix A - SOP SUMMARY

Collection, Preservation, and Hold Times

Container	**Aqueous**: Minimum 250mL plastic or glass bottle with a plastic or Teflon-lined lid. **Soils**: Minimum 250mL plastic or glass bottle with a plastic or Teflon-lined lid. If other metals are being tested, the aliquot form mercury may be taken from the same container
Preservation	**Aqueous**: HNO3 to pH <2 in the field If dissolved mercury is required, filter the samples before preservation. **Soils**: No chemical preservation required
Storage	**Aqueous**: Room temperature if properly preserved **Solids** should be stored at 4°C (<6°C , but not frozen) from collection until preparation.
Hold Time	**Aqueous and Soils**: Aqueous and Soils: Samples must be analyzed within 28 days of collection.

Wastes are treated in the same manner as soils.

ANALYTICAL SEQUENCE	
Instrument Startup	Turn on the mercury analyzer according to the instrument manufacturer's recommendations. Allow the mercury lamp Proper warm-up time. Inspect and change pump tubes and drying tubes as needed Check and align lamp and cell According to the instrument manufacturers recommendations.
Initial Calibration	Beginning with the blank, calibrate with the blank and 5 standards. One standard must be at or below the RL.
Initial Calibration Verification (ICV/ICB)	Analyze an initial calibration verification solution at the beginning of the analysis run. The ICV Solution must come from a source other than the calibration source. Analyze a calibration blank after the ICV.
Continuing Calibration Verification (CCV/CCB)	Analyze a standard with a concentration at or near mid-range levels of the calibration. The CCV should be analyzed every 10 samples and at the end of the analysis run. The CCV and ICV may be the same solution. Analyze a calibration blank after every CCV.
Detection Limit Check Solution	At the beginning of the analysis run, verify the accuracy at the RL by analyzing a standard with a concentration at or below the required RL.
Post Digestion Spikes/Serial dilution	At a minimum of once per analytical batch, verify the absence of matrix interference by analyzing a post digestion spike and a serial dilution.

Appendix A - SOP SUMMARY

QC CRITERIA

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	1 blank and 5 standards Correlation > 0.995	Recalibrate
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	SW846 = within ± 10% 245.1 = within ± 5%	Recalibrate
Continuing Calibration Verification Standards (CCV)	At the beginning and end of the analysis and every 10 samples.	SW846 = within ± 20% 245.1 = within ±10%	Terminate the analysis, correct the problem and reanalyze all samples since the last compliant CCV.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be less than the required RL.	SW846 = terminate the analysis, Correct the problem and reanalyze all samples since the last compliant CCB.
RL standard (detection limit standard CRA)	After every calibration but not before the ICV.	50-150% of true value	Recalibrate.
Laboratory control sample (LCS)	One per batch of twenty or fewer samples	LQM Limits	Redigest and reanalyze batch
Preparation Blank - SW846	One per batch of twenty or fewer samples	Result < required RL.	Re-digest and reanalyze batch (if sample result >20X the blank, the sample does not have to be re-digested/reanalyzed)
MS/MSD - SW846	One set per batch of twenty or fewer samples	%Rec = 80 – 120% %RPD = < 20%	Flag and report data
MS – 245.1	MS added to a minimum of 10% of samples	%Rec = 70 - 130%	Flag and report data
Serial Dilution Analysis (1+4 dilution)	One per batch of twenty or fewer samples	If sample is at least 25 times the instrument detection limit the serial dilution, corrected for the dilution factor, should agree within +/- 10% of the undiluted sample. (Section 10.8)	Evaluate the post-digestion spike.
Post Digestion Spikes	One per batch of twenty or fewer samples	%Rec = 85 - 115% (Section 10.6)	Check for interference source and reanalyze samples, dilute all samples, or analyze all samples by MSA.

SEVERN TRENT STL

DIGESTION PROCEDURES FOR ICP & ICP/MS: TOTAL METALS IN SOILS, SEDIMENTS, WASTES, TISSUES, AND OILS

(METHOD: EPA 3050B)

Technical Approval:

Andrea Teal   01/30/04
Date

Title: QA Manager
STL Savannah

Safety Approval:

Ernest B. Walls   02/03/04
Date

Title: EHSC
STL Savannah

1.0 SCOPE AND APPLICATION

The purpose of this SOP is to describe the procedures used to digest soils, sediments, wastes, biological tissues, and oil samples prior to analysis by ICP (SOP ME70: *Elements by ICP*) or ICP-MS (SOP ME74: *Elements by ICP-MS*).

The reporting limit (RL), the method detection limit (MDL), and the accuracy and precision limits associated with these procedures are listed in the analytical SOPs and/or the Laboratory Quality Manual (LQM) prepared by and for STL Savannah.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 A known weight (approximately 1g) of the well-mixed sample is transferred to a suitable digestion vessel. The sample is digested with aliquots of nitric acid and hydrogen peroxide to break down the organics present in the sample. After the sample has been digested, as evidenced by a clear, pale yellow digestate, HCl is added to give an approximate acid concentration of 1% HCl and 5% HNO_3 Then the sample digest is diluted to 100mL with reagent water.

A smaller weight of sample may be digested and the sample brought to a final volume that is proportional to the 1g sample to 100mL final volume ratio. For example, if 0.50g is digested, the final volume of the digestate must be 50mL to achieve the same reporting limits

2.2 Definitions – Refer to SOP AN99: *Definitions, Terms, and Acronyms* for a complete listing of applicable definitions.

Digestate - the digested sample
ICP - inductively coupled (argon) plasma
HCl –hydrochloric acid
HNO3 – nitric acid

2.3 The SOP is based on the guidance in SW-846 Method 3050B.

3.0 SAFETY

Employees must abide by the policies and procedures in the Corporate Safety Manual, the Waste Management SOP, and this document.

3.1 Specific Safety Concerns or Requirements

Nitric and hydrochloric acids are extremely hazardous as oxidizers, corrosives, poisons, and are reactive. Inhalation of the vapors can cause coughing, choking, irritation of the nose, throat, and respiratory tract, breathing difficulties, and lead to pneumonia and pulmonary edema. Contact with the skin can cause severe burns, redness, and pain. Nitric acid can cause deep ulcers, and staining of the skin to a yellow or yellow-brown color These acid vapors are irritating and can cause damage to the eyes. Contact with the eyes can cause permanent damage.

Samples that contain high concentrations of carbonates or organic matter, or samples that are at elevated pH can react violently when acids are added. Acids must be added to samples under a hood to avoid splash/splatter hazards and/or possibly toxic vapors that will be given off when the samples are acidified.

3.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes Contact may cause severe burns or permanent eye damage.
Nitric Acid	Corrosive Oxidizer Poison	2ppm-TWA 4ppm-STEL	Nitric acid is extremely hazardous; it is corrosive, reactive, an oxidizer, and a poison. Inhalation of vapors can cause breathing difficulties and lead to pneumonia and pulmonary edema, which may be fatal. Other symptoms may include coughing, choking, and irritation of the nose, throat, and respiratory tract. Can cause redness, pain, and severe skin burns. Concentrated solutions cause deep ulcers and stain skin a yellow or yellow-brown color. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

4.0 INTERFERENCES

Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

The following table lists the routine sample containers, preservatives, and storage and holding time information:

MATRIX	ROUTINE CONTAINER	PRESERVATIVE	STORAGE/ HOLD TIME
Soils and sediments	500-mL plastic	None	<6°C but not frozen
Wastes and Oils	500-mL plastic or glass*	None	Ambient or <6°C but not frozen
Biological Tissues	500-mL plastic or glass	None	Frozen until the time of sample preparation

*Some organic wastes may destroy plastic containers

6.0 APPARATUS AND MATERIALS

6.1 Hot plate or digestion block-capable of maintaining a sample temperature of 95 ± 5°C: The temperature of the hot plate or digestion block must be monitored and recorded each day samples are digested. The temperature is measured in a beaker or digestion vessel containing reagent water.

6.2 Digestion vessels, appropriate volume for use with digestion block

6.3 Teflon or Pyrex beakers, appropriate volumes, recommend 150-mL or 250-mL beakers for use with hot plates

6.4 Watch glasses, for use with beakers (block digestion vessels do not require watch glasses)

6.5 Teflon vials – 25-mL

6.6 Volumetric flasks - appropriate volumes

6.7 Graduated cylinder - appropriate volume

6.8 Pipettes

6.9 Analytical balance

6.10 Top-loading balance

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability*.

7.1 Reagent water-lab generated deionized water. ASTM Type I or Type II. The conductivity must be checked daily in accordance with SOP AN35: *Conductivity Checks for Laboratory Deionized Water*.

7.2 Nitric acid (HNO_3) - reagent grade. The manufacturer's certification assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.3 Nitric acid solution (1:1) - Measure 500mL of reagent water into a 2-L beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Carefully and slowly, add 500mL of concentrated nitric acid (HNO_3) to the reagent water in the beaker on the magnetic stir plate. Transfer the reagent to a labeled container suitable for storing acidic solutions. Do not store reagents in volumetric glassware. Prepare this reagent as needed.

CAUTION: HEAT WILL EVOLVE AS THE NITRIC ACID MIXES WITH THE WATER. THIS SOLUTION WILL CAUSE SKIN BURNS AND DESTROY UNPROTECTED CLOTHING.

7.4 Hydrochloric acid (HCl) - reagent grade. The manufacturer's certification sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.5.1 Hydrochloric acid solution (1:1) - Measure 500mL of reagent water into a 2-L beaker. Place the beaker on a magnetic stir plate and add a Teflon stir bar to the beaker. Carefully and slowly, add 500mL of concentrated hydrochloric acid (HCl) to the reagent water in the beaker on the magnetic stir plate.

Transfer the reagent to a labeled storage container suitable for acidic solutions. Do not store reagents in volumetric glassware. Prepare this reagent as needed

CAUTION: HEAT WILL EVOLVE AS THE HYDROCHLORIC ACID MIXES WITH THE WATER. HYDROCHLORIC ACID HAS A SUFFOCATING ODOR AND MUST BE USED UNDER THE HOOD. THIS SOLUTION WILL CAUSE SKIN BURNS AND DESTROY UNPROTECTED CLOTHING. PREPARE THIS SOLUTION UNDER A HOOD.

7.6 Hydrogen peroxide, 30% - reagent grade. Check for impurities by the analysis of a method blank.

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SOP AN41: Standard Materials Traceability. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation*.

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation.

8.1 Determine the volume of standard to be prepared and the volume of the stock standard needed to make the spiking solutions. The following equation can be used:

$$Ci \otimes Vi = Cf \otimes Vf$$

$$Vi = \frac{Cf \otimes Vf}{Ci}$$

where
Vi = volume of stock standard needed to prepare the spiking solution (mL)
Ci = concentration of stock solution (µg/mL)
Cf = concentration of spiking solution to prepare (µg/mL)
Vf = volume of spiking solution to prepare (mL)

The concentration can be expressed in whatever terms the analyst finds most convenient - µg/L, µg/mL, mg/L, etc. The units must be the same for Ci and Cf.

ICP Matrix Spiking Solution 1 is a purchased solution containing the following elements: aluminum, arsenic, barium, selenium, thallium at 200mg/L; iron at 100mg/l; cobalt, magnesium, nickel, lead, strontium, vanadium, antimony at 50mg/L; copper at 25mg/L; chromium at 20mg/L; and silver, beryllium, cadmium at 5mg/L. Store this solution at room temperature.

8.2.2 Preparation of the ICP Matrix Spiking Solution 2

Add 20mL to 30mL of reagent water to a clean 100-mL volumetric flask. Add 1mL of concentrated nitric acid (HNO_3) and 5mL of hydrochloric acid (HCl) to the volumetric flask. The standard will have an acid concentration of 1% HNO_3 and 5% HCl when diluted to volume.

Add the volumes of the stock standards given in the following table to the volumetric flask:

Element	Conc. of Stock (mg/L)	Vol. of Stock (mL)	Final Vol. (mL)	Conc. of std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0	100	500
Magnesium (Mg)	10000	5.0	100	500
Molybdenum (Mo)	1000	5.0	100	50
Potassium (K)	10000	5.0	100	500
Sodium (Na)	10000	5.0	100	500
Strontium (Sr)	1000	5.0	100	50
Tin (Sn)	1000	10	100	100
Titanium (Ti)	1000	10	100	100

Dilute to a final volume of 100mL with reagent water. Store the standard at room temperature. Prepare this solution every six months or sooner if needed or required.

9.0 SAMPLE PREPARATION

This digestion procedure is used for the preparation of soil, sediment, waste, tissues, and oil samples for the determination of total metals analyzed by ICP, ICP-MS. This digestion procedure may not be suitable for some analytes that will be analyzed by graphite furnace atomic absorption (GFAA) because HCl can cause interferences during furnace atomization.

9.1 Weigh 1.0-1.2g (wet weight) of a homogeneous sample into a 125-mL Teflon beaker or other suitable digestion vessel. The lab may weigh a larger aliquot equal to 1.0g of sample on a dry weight basis, if required.

NOTE: A smaller weight of sample may be digested and the sample brought to a final volume that is proportional to the 1g sample to 100mL final volume ratio. For example, if 0.50g is digested, the final volume of the digestate should be 50mL to achieve the same reporting limits; if 0.1g is digested, the final volume of the digestate should be 10mL. If the sample weight to final volume ratio is greater than 1:100, the reporting limits will be higher than those listed in the LQM.

9.1.1 To homogenize a soil sample, the sample may be vigorously stirred in the sample container or transferred to a plastic "baggie" and thoroughly mixed by kneading the container. After the sample is homogenized, return only enough sample to the original container to fill it three-fourths full. This will allow the sample to be stirred and homogenized if additional aliquots of the sample are required. Place the discarded sample in a containerized waste receptacle for disposal.

9.1.2 If the sample is a solid material, break up the solid in the baggie by hitting the sample with a hammer or other suitable crushing device. Contact the immediate supervisor if the matrix is difficult to break up or is difficult to mix.

9.2 Add 1.0mL of the appropriate spiking solution to the designated laboratory control spikes. The LCS/LCSD are prepared by weighing 1g aliquots of the "blank soil" into labeled beakers or digestion vessels.

9.3 Add 1.0mL of the appropriate spiking solution to the designated matrix spike samples. The MS/MSD are prepared by weighing 1.0-1.2g of the sample chosen for the matrix spike into labeled beakers or digestion vessels. The lab may weigh a larger aliquot equal to 1.0g of sample on a dry weight basis for the MS/MSD or may use a smaller weight if the final volume of the digestate is adjusted or if higher reporting limits are acceptable.

9.4 Record the following information on the digestion log:

- date
- analyst's initials
- beaker ID#
- sample identification
- the weight of sample digested
- batch identification
- fume hood #
- temperature of the hot plate or digestion block (daily)
- the lot number of the acids used for the digestion
- the lot number of the ICP spiking solutions
- the time that the digestion was started
- the SOP/method number

NOTE: THE DIGESTION BATCH CONSISTS OF TWENTY OR FEWER FIELD SAMPLES AND THE ASSOCIATED QC ITEMS. A DIGESTION BATCH IS NOT TO EXCEED 20 FIELD SAMPLES. EVERY DIGESTION BATCH WILL HAVE A METHOD BLANK, A LABORATORY CONTROL SAMPLE (LCS), A MATRIX SPIKE AND A MATRIX SPIKE DUPLICATE (IF THERE IS SUFFICIENT SAMPLE FOR THE MS/MSD). PERFORM THE LCS IN DUPLICATE IF THE MS/MSD CANNOT BE PERFORMED. SOME CLIENTS MAY REQUIRE SAMPLE DUPLICATE INSTEAD OF MSD. THE METHOD BLANK IS PERFORMED WITH THE REAGENTS USED FOR THE DIGESTION. LAB SPIKES FOR SOIL MATRICES WILL BE PERFORMED USING 1-G ALIQUOTS OF BLANK SAND

9.5 Add 5mL of reagent water and 5mL of concentrated HNO_3 to each beaker, mix, and cover the beaker with a watchglass. A watchglass is not used with the digestion block vessels.

9.6 Carefully heat the beaker until a gentle reflux is achieved. The sample is not heated to boiling; that is, bubbles are not formed in the liquid in the bottom of the beaker. The sample/acid solution is refluxing when the liquid evaporates and drops of liquid condense on the watch glass and the sides of the beaker and fall back into the beaker. Do not allow the samples to boil. Reflux for 10-15 minutes.

9.7 Remove the beakers from the hot plate or digestion block and allow the beakers to cool to room temperature. Add 5mL of concentrated HNO_3 to each sample. Replace the watchglass and return the beakers to the hot plate or digestion block. Carefully heat the beaker until a gentle reflux is achieved. Reflux the samples for 30 minutes. Do not allow the samples to boil.

9.8 Repeat the procedure in Section 9.7 with a second 5mL portion of concentrated HNO_3 if brown fumes are given off. Repeat Section 9.7 until no brown fumes are given off.

9.9 Evaporate the sample digestate to approximately 10mL. Do not allow the bottom of the beaker to go dry during the evaporation. Allow the sample to cool to room temperature before continuing onto the next step.

NOTE: If the sample is still warm when the 30% H_2O_2 (hydrogen peroxide) is added in the next step, the sample may "boil over" and the entire process must be started over.

9.10 Add 2mL of reagent water to each beaker. Slowly and carefully add 3mL of 30% H_2O_2 to each beaker. It is very important to add the hydrogen peroxide slowly to prevent loss of sample due to vigorous effervescence. Return the beakers to the hot plate or digestion block and heat until the effervescence subsides. Cool the beaker after the effervescence subsides.

9.11 Continue to add 30% H_2O_2 in 1-3mL aliquots to the sample digestate until the effervescence is minimal or until the general appearance of the digestate is unchanged. Warm the sample digestate after each addition of H_2O_2 on the hot plate or digestion block.

NOTE: Do not add more than 10mL of hydrogen peroxide to each sample.

9.12 After the last addition of peroxide, reduce the volume of the digest to 5-10mL without boiling and without allowing the bottom of the beaker to go dry. Add 10mL of concentrated HCl to each sample digestate. Replace the watch glass, return the beakers to the hot plate or digestion block, and reflux the sample digestates for 10-15 minutes.

9.13 Wash down the inside of the beaker and the watchglass with reagent water. Dilute the sample digestate to 100mL with reagent water.

9.14 Record the analyst's initials, the final volume of the sample digestate, and the date that the digestion was completed in the digestion logbook. The sample is now ready for analysis.

10.0 ANALYTICAL PROCEDURES

The digestion procedure is described in Section 9.0. The analytical procedures are given in SOP ME70: *Elements by ICP* or SOP ME74: *Elements by ICP-MS*.

11.0 DATA ANALYSIS AND CALCULATIONS

Calculations for the determination of metals by ICP are given in the associated analytical SOPs (SOP ME70 or SOP ME74).

12.0 QUALITY CONTROL AND DATA ASSESSMENT

12.1 The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

SOP AN02: *Analytical Batching and Evaluation of QC Data* and the associated analytical SOPs contain guidance for evaluating the QC in an analytical batch. The accuracy and precision limits are published in the current LQM.

12.2 Corrective Action for Out-of-Control Data

When the quality control parameters do not meet the criteria set forth in this SOP, corrective action must be taken in accordance with SOP CA85: *Nonconformance and Corrective Action Procedures*. CA85 provides contingencies for out-of-control data and gives guidance for exceptionally permitting departures from approved policies and procedures.

13.0 METHOD PERFORMANCE

The Reporting Limits (RL), the Method Detection Limits (MDL), and accuracy and precision limits associated with these methods are given in the current revision of the Laboratory Quality Manual prepared by and for STL Savannah.

13.1 Initial and Continuing Demonstration of Capability

Initial and continuing demonstration of capability must be performed in accordance with SOP *CA92: Procedure for Initial and Continuing Analyst Demonstration of Capability.*

13.2 Method Detection Limit

The method detection limit must be determined for each analyte in accordance with SOP CA90: *Procedures for the Determination of Method Detection Limit (MDL).*

14.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

Refer to SOP AN53: *Maintenance Procedures for Laboratory Instrumentation* for routine preventive maintenance and the manufacturer's guides for trouble-shooting items.

The temperature of the hot plate or digestion block must be monitored daily. If the temperature required for sample preparation cannot be maintained, the heating device must be removed from service and repaired or replaced.

15.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All waste will be disposed of in accordance with Federal, State and Local regulations. Follow the guidance for disposal in SOP CA70: *Waste Disposal.* Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment.

Excess samples, reagents, and standards must be disposed in accordance with SOP CA70: *Waste Management.*

15.1 Waste Streams Produced by the Method

The following waste streams are produced when this method is carried out.

Excess soil samples from homogenization procedure - Transfer to TCLP container for characterization in hazardous waste department.

Excess soil and solid samples – Dispose according to characterization on sample disposal sheets. Transfer non-hazardous samples to TCLP container for characterization in hazardous waste department. Transfer hazardous samples (identified on disposal sheets) to waste department for disposal.

Acidic sample digestions – Neutralize before disposal into drain/sewer system.

Excess oil samples – Transfer to waste department for storage/disposal.

16.0 REFERENCES

STL Savannah's *Laboratory Quality Manual (LQM)*, current revision

Severn Trent Laboratories' *Quality Management Plan (QMP), current revision*

Test Methods for Evaluating Solid Waste, Third Edition, SW-846; EPA Office of Solid Waste and Emergency Response: Washington, DC. (including Update III)

17.0 TABLES, DIAGRAMS, AND VALIDATION DATA

There are no tables, diagrams, or validation data included in this SOP.

SEVERN
TRENT
SERVICES

ELEMENTS BY ICP (200.7 and 6010B)

Approved by:

R. Wayne Robbs ____ 7 March 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa West

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures to determine the concentration of various elements by inductively coupled plasma (ICP) atomic emission spectroscopy. This method contains the analytical procedures for the determination of metals in surface and ground water, wastewater, soil, sediment, leachate (EP or TCLP), and waste samples after digestion.

1.2 Table 1 lists the elements that may be determined by ICP and the characteristic wavelength used for each element. The reporting limit (RL) for each element, the method detection limit (MDL) for each element, and the accuracy and precision criteria for each element are in the Laboratory Quality Manual (LQM) prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Prior to analysis by ICP, the sample must be solubilized or digested using the sample preparation method appropriate to the matrix. Sample digestates are aspirated and nebulized into a spray chamber. A stream of argon gas carries the sample aerosol through the innermost of three concentric tubes and injects it into the middle of the donut-shaped plasma. The sample elements are dissociated, atomized, and exited to a higher energy level. As the elements fall to a lower energy level, radiation characteristic of the elements present in the plasma is emitted. The light is directed through an entrance slit, dispersed by the diffraction grating, and projected on to the photomultiplier tube (PMT). The PMTs, located behind the exit slits, convert the light energy to an electrical current. This signal is then digitized and processed by the data system. Background correction is required for trace element determination.

2.2 Definitions

ICP -inductively coupled (argon) plasma; sometimes referred to a "ICAP"
TCLP-toxicity compound leaching procedure
EP (tox)-extraction procedure (toxicity)
Analytical Spike or Post-Digestion Spike - addition of a known concentration of analyte to an aliquot of sample after the preparation steps have been performed
RL - reporting limit, the lowest calibration standard or the sample equivalent of the lowest calibration standard; published in LQM or project-specific quality assurance plan (QAPP); sometimes referred to as the "practical quantitation limit(PQL).
MDL - method detection limit, the concentration that can be reported with 99% confidence that the result is greater than zero; published in LQM

2.3 This method is based on EPA Method 200.7 and SW-846 Method 6010B. Note that EPA has promulgated two versions of method 200.7-one for NPDES samples and one for drinking water. The calibration sequence for drinking water by 200.7 requires a multi-point curve with a minimum of three standards and a calibration blank.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 Each digestion lab must have acid spill kits. These kits must be located in a highly accessible area of the lab. Each digestion lab must be equipped with a properly working shower.

3.3 The standards and reagents used to prepare the standards in this method should be treated as potential hazards. Lab coats, gloves, and other protective equipment should be used when preparing and using the standards and reagents.

3.4 The Material Safety Data Sheets (MSDS) for each reagent and standard are located in each laboratory. These sheets denote the type of hazard that each reagent poses, the safe handling instructions for these compounds, and first aid instructions.

4.0 INTERFERENCES

4.1 Spectral interferences are caused by (1) the overlap of a spectral line from another element, (2) unresolved overlap of molecular band spectra, (3) background contribution from continuous phenomena, and (4) stray light from the line emissions of highly concentrated elements.

4.1.1 Spectral overlap may be compensated for by the use of inter-element correction factors.

4.1.2 Background contribution and stray light can be compensated for by a background correction adjacent to the analyte line.

4.2 Physical interferences are effects associated with the sample nebulization and transport processes. Changes in viscosity can cause significant inaccuracies, especially in samples containing high concentrations of dissolved solids or high acid concentrations. If physical interferences are present, they must be reduced by diluting the sample digestate, by using a peristaltic pump, or by using the method of standards additions(MSA), or use of an internal standard

4.3 Contamination of the sample can occur when the preparation glassware and/or reagents contain the target elements. Reagent blanks (method blanks) must be analyzed as a check on contamination due to the sample digestion.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

5.1 Aqueous Samples

5.1.1 Liquid samples are routinely collected in 250-mL or 500-mL plastic containers. The sample is preserved with HNO_3 to a pH <2. The sample must be digested and analyzed within 6 months of collection. Samples may be stored at room temperature.

5.1.2 Samples for dissolved metals should be filtered in the field before acid is added to the sample. If the sample is to be filtered in the lab, no preservative is added to the sample until the sample is filtered.

5.2 Soil/Sediment Samples
Soil and sediment samples are routinely collected in 500-mL plastic containers. The sample is iced at the time of collection and is stored in the lab at 4C (less than 6C but not frozen) until time of digestion and analysis. The sample must be digested and analyzed within 6 months of collection.

5.3 TCLP or EP Toxicity Leachate Samples
The leachate is transferred to a plastic container after the extraction procedure. The sample is preserved with HNO_3 to a pH <2. The leachate sample must be digested and analyzed within 6 months of completion of the leaching procedure.

5.4 Waste Samples
Waste samples are routinely collected in 500-mL plastic containers. The sample must be digested and analyzed within 6 months of collection.

6.0 APPARATUS AND MATERIALS

6.1 Thermo Jarrell Ash TJA ICAP61E-trace, or other suitable inductively coupled plasma emission spectrometer with data system

6.2 Argon gas supply and appropriate fittings

6.3 Cooling water supply

6.4 Peristaltic pump

6.5 Volumetric flasks

6.6 Pipettes

7.0 REAGENTS

Reagents are tracked in accordance with STL SOP AN44:*Reagent Traceability.*

7.1 Reagent water-lab generated deionized water, ASTM Type I or Type II. The conductivity is monitored in accordance with STL SOP AN35.

7.2 Nitric acid (HNO_3)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

7.4 Hydrochloric acid (HCl)-reagent grade. The assay sheet of each lot of acid received into the lab must be reviewed to make sure that the quality of the acid is sufficient for trace analysis of metals.

8.0 STANDARDS

Calibration and spike solutions are prepared from either certified stock solutions or from stock solutions purchased from vendors. Certificates of analysis or purity must be received with all neat compounds or stock solutions. All preparation steps must be in accordance with STL SOP AN41: *Standard Materials Traceability.* SOP AN43 contains guidance for the preparation of standards.

8.1 Recommended concentrations for the calibration standards are given in Table 1. Appendix A contains examples for the preparation of the initial calibration and calibration verification standards for both 6010 and 200.7. if the laboratory uses "recipes' other than those listed in Appendix A, the recipe must be documented in the standard material traceability logbook or as controlled posting. All standards must have be prepared in 5% hydrochloric acid and 1% nitric acid by volume.

NOTE: Standards must be prepared every six months "or sooner if needed or required." "If needed" means the standard has been exhausted; "if required" means that the standard does not meet the QC criteria.

8.2 Preparation of the Linearity Check Solutions

The linearity check solutions are prepared individually according to the following equation:

$$Vs = \frac{Vlc \otimes Clc}{Cs}$$

where
Vs = volume of stock standard (mL)
Cs = concentration of stock standard (mg/L)
Vlc = volume of linearity check standard to prepare (mL)
Clc = concentration of linearity check standard to prepare (mg/L)

The linearity check solutions are prepared at the concentrations specified in Table 1. Prepare sufficient volume to perform the linearity check, maintaining the hydrochloric acid concentration at 5% by volume and the nitric acid concentration at 1% by volume.

9.0 SAMPLE PREPARATION

The sample preparation and digestion procedures are listed in the following SOPs:

MATRIX	SOP
Aqueous and leachate samples	ME50
Soils and Sediments	ME51
Wastes and oils	ME51

10.0 ANALYSIS PROCEDURE

The analytical sequence, including standardization and calibration verification, is included in the SOP Summary in Appendix A. The SOP Summary also included the acceptance criteria for QC, including recommended corrective actions.

10.1 Initial Calibration/Standardization

10.1.1 Turn the ICP on and allow it to become thermally stable before beginning to analyze the calibration standards. It will take about an hour for the instrument to warm up. If optics were turned off, allow 2 hours warm up time.

10.1.2 Run the "Automatic Profile" program. The "automatic profile" of the instrument should be checked twice a day to compensate for changes in air pressure, humidity, and temperature. If the environment of the instrument is such that daily changes in the instrument profile are extreme, the instrument should be "profiled" every few hours.

10.1.3 Analyze the calibration standards and calibrate the ICP. ***If using a multi-point calibration, use the Calibration/Analysis and Curvefit programs to calibrate the instrument.***

10.1.4 The highest concentration calibration standard is reanalyzed after the instrument is standardized as an "unknown". The results for the re-analysis of the highest concentration calibration standard must be within +/- 5% of the true value for each target analyte. If the result for any target analyte is outside of this range, the ICP may need to be "profiled" and the standardization/calibration repeated.

10.1.5 The QC Check standards (ICV) and the Calibration Blank (ICB) are analyzed as a check on the instrument calibration.

10.1.5.1 (EPA Method 6010) The results for the target compounds in the initial calibration verification (ICV) must be within the +/- 10 % of the true value.

10.1.5.2 (EPA Method 200.7) The results for the target compounds in the initial calibration verification (ICV) must be within the +/-5.0 % of the true value. **When performing 200.7 work, note that this solution should be prepared fresh weekly.**

10.1.5.3 (EPA 6010/200.7) The results for the target compounds in the initial calibration blank (ICB) must be less than the RL.

10.1.6 The RL/PQL Check Solution is analyzed to demonstrate that the ICP is capable of detecting the target compounds at or near the reporting limit (RL). The determined concentration must within +/- 50% of the true concentration.

10.1.7 The ICP Interference Check Sample is analyzed. The concentrations of the target analytes must be within 20% of the true concentrations. Pay particular attention to false positives and false negatives for elements not present in the interference check solutions.

10.2 Continuing Calibration Verification (CCV)

10.2.1 The calibration of the ICP must be verified every 10 samples by the analysis of the analysis of the QC Check Solutions (CCV) and the Calibration Blank (CCB).

10.2.1.2 (EPA Method 6010/200.7-DW) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/- 10 % of the true value.

10.2.1.2 (EPA Method 200.7-NPDES) The results for the target compounds in the continuing calibration verification (CCV) must be within the +/-5.0 % of the true value.

10.2.1.3 (EPA 6010/200.7) The results for the target compounds in the continuing calibration blank (CCB) must be less than the Reporting Limit (RL).

10.2.2 ICP Interference Check Solution and the RL check solution are analyzed at the beginning and end of each analytical sequence.

10.3 Sample Analysis

10.3.1 The samples are analyzed only after the ICB/CCB and ICV/CCV criteria are met.

10.3.2 The samples are analyzed in a sequence as follows:

INSTRUMENT WARM-UP
PROFILE
INITIAL CALIBRATION (STANDARDIZATION/CALIBRATION OF THE ICP)
REANALYSIS OF HIGH CONCENTRATION CALIBRATION STANDARD AS A SAMPLE
INITIAL CALIBRATION VERIFICATION (ICV)
INITIAL CALIBRATION BLANK (ICB)
DETECTION LIMIT CHECK SOLUTION
ICP INTERFERENCE CHECK SOLUTION A (ICSA)
ICP INTERFERENCE CHECK SOLUTION AB (ICSAB)
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CONTINUING CALIBRATION VERIFICATION (CCV)
CONTINUING CALIBRATION BLANK (CCB)
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB
10 SAMPLES
CCV
CCB

The analytical sequence must end with the analysis of the detection limit check standard, ICSA, ICSAB, CCV and CCB. The 10 samples include all QC samples/standards with the exception of CCVs and CCBs.

10.3.3 Determine the concentration of the samples and QC items using the procedures of Section 11.

10.3.3.1 If the concentration of a sample is above the linear range of the ICP, the sample digestate must be diluted and reanalyzed.

10.3.3.2 The amount of sample digestate needed to prepare the desired dilution is determined form the following equation:

$$V_{digest} = \frac{Vf_{vol}}{DF}$$

where
Vf_{vol} = final volume of diluted sample (mL)
V_{digest} = volume of sample digestate used to make the dilution (mL)

10.3.3.3 The dilution factor is calculated as follows:

$$DF = \frac{Vf_{vol}}{V_{digest}}$$

where
Vf_{vol} = final volume of diluted sample extract (mL)
V_{digest} = volume of sample extract used to make the dilution (mL)

NOTE: The following examples are based on a final volume of 100mL. It may be more convenient to prepare dilutions at smaller final volumes.

EXAMPLE
A sample digestate is analyzed and one of the target analytes exceeds the linear range of the ICP. 1.0mL of the digestate is added to a 100mL volumetric flask and the extract brought up to volume with reagent water. What is the dilution factor?

$$DF = \frac{100mL}{1.0mL} = 100$$

Dilutions must be prepared in reagent water containing 5% hydrochloric acid and 1% nitric acid by volume.

Some samples may require multiple dilutions; that is, a dilution of a dilution will have to be made. In this case, the final dilution factor is the product of the individual dilutions.

10.4 Dilution QC Check
A dilution is prepared and analyzed on one sample per batch to determine if matrix interferences are present.

10.4.1 Select a sample digestate that contains one or more target analytes at a concentrations greater than 10X the reporting limit.

10.4.2 Dilute the digestate by a factor of 5 (DF=5) and analyze the dilution using the same procedures used for the un-diluted aliquot.

10.4.3 Compare the results of the diluted and un-diluted aliquots of sample digestate.

10.4.4 If the results of the dilution are within $\pm$ 10% of the results of the undiluted sample, no matrix interference is present. If the results differ by greater than $\pm$ 10%, a matrix interference should be suspected and the sample digestate should be subjected to a post-digestion spike (see section 10.4).

If the concentration of the analyte in the sample is not at least 50 times the instrument detection limit, evaluate the post-digestion spike.

10.5 Post-digestion Spike QC Check

A post-digestion spike is performed on one sample per analytical batch to determine if matrix interferences are present. This post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration is not at least 50 times the instrument detection limit. This should be the same sample selected for dilution in 10.3, above.

10.5.1 Transfer 10mL of a digestate to a suitable vial.

10.5.2 Spike the sample with 0.10mL of ICP Matrix Spike I and 0.10mL of ICP Matrix Spike II. The theoretical concentration of the post digestion spike is the same as the LCS or MS if the volume of spiking solution is discounted.

10.5.3 Analyze the spiked aliquot and an un-spiked aliquot (the un-spiked may have been analyzed previously and does not need to be reanalyzed).

10.5.4 Calculate the percent recovery of the post digestion spike:

$$\%REC = \frac{C_{ps} - C_s}{C_2} \times 100$$

where

Cps = concentration of post digestion spike (ug/L)
Cs = concentration of un-spiked sample (ug/L)
C2 = theoretical concentration of spike (ug/L)
(See 10.2.5.2)

10.5.5 Evaluate the recovery using the following decision matrix. Limits for post digestion spikes are 75-125% recovery.

Result of Post Digestion Spikes	Action
Within 75-125% limits	None
>125% recovery	Repeat analysis. Remake spiking solutions, re-spike, and reanalyze. Reanalyze un-spiked sample
<75% recovery but >50% recovery	1) Dilute and re-spike. Elevate RL accordingly (for all associated samples). 2) Spike and evaluate all associated samples. 3) Spike and evaluate all associated samples by single point MSA 4) Qualify all associated samples
<50% recovery	Dilute digestate and repeat spike. Treat all samples associated with spike in the same manner as the spiked sample (i.e., spike or dilute samples) If recoveries are not 75-125%, analyze all associated samples by single point MSA. Note – high level of target analytes may inhibit spike recovery. Consult the supervisor in events where high levels of targets appear to be interfering

Note: The >50% recovery of the post digestion spike is a benchmark below which samples may be biased high if corrected for spike recovery.

10.5.6 The post digestion spike and the method of standard additions must not be applied to samples analyzed at a dilution that produces a significant negative response. The analyst must use good judgement when evaluating data where the sample response is negative. Where a significant negative response is present, the digestate should be diluted and reanalyzed to determine the extent of the matrix interferences.

10.6 Single Point Method of Standard Additions

Two identical aliquots of the sample digest, Vx, are taken. One aliquot is spiked with a solution of known concentration, Cs. The second aliquot is analyzed un-spiked (the small volume of standard added to the spiked sample should be disregarded). The concentration of both aliquots are measured and the sample concentration, Cx, is calculated:

$$C_x = \frac{S_2 V_s C_s}{(S_1 - S_2) V_x}$$

where

S_1 = absorbance or concentration of the spiked aliquot
S_2 = absorbance or concentration of the un-spiked aliquot
Vs = Volume of spike solution

Example:		
	Sample concentration (S_2):	523 ug/L.
	Spike solution concentration (C_s):	50,000 ug/L
	Volume of spike solution (V_s):	0.10mL
	Volume of sample aliquots (V_x):	10mL
	Spiked sample concentration (S_1):	951 ug/L

C_x = [(523)*(0.10)*(50,000)]/[(951-523)*10)] = [2,615,000]/[4280] = 611 ug/L

10.7 Determination of Linear Range of the ICP

The linear range must be determined a minimum of once per year. Divisions performing CLP analyses are required to determine and document the linear range quarterly. Documentation of the linear range study must be kept on hand and be available for inspection. A summary of the linear range study must be available to the bench analyst.

10.7.1 Profile and calibrate the ICP as described in Section 10.1

10.7.2 Prepare individual standards at concentrations that are expected to define the linear range of the instrument. Use the concentrations in Table 1 for guidance. The calibration standards and the linear range standards should be matrix matched; that is, they have the same percentage of hydrochloric and nitric acids.

10.7.3 Analyze the standards following the analytical sequence described in Section 10.3. Verify the calibration after every 10 analyses.

10.7.4 Compare the concentration of the linear range standard with its true concentration.

$$PercentDifference = \left|\frac{Ccal - Ctrue}{Ctrue}\right| \otimes 100$$

where
Ccal = concentration determined from analysis
Ctrue = true concentration of the standard

If the percent difference is less than or equal to 5%, the linear range is confirmed at that concentration. If the percent difference is greater than 5%, repeat the analysis with a lower concentration.

The linear range may be extended by analyzing higher standards and evaluating the results against the 5% difference criterion. The linear range of the ICP for an analyte is the highest standard of that analyte that meets this criterion.

11.0 DATA ANALYSIS/CALCULATIONS

11.1 Aqueous and Leachate Samples

Aqueous samples are routinely reported in mg/L while the ICP is routinely calibrated in ug/L. If the results are reported in ug/L, the conversion factor is omitted from the calculation.

11.1.1 The concentration of the target analyte in liquid samples is calculated as follows:

$$Concentration\ (mg/L) = ug/L(from\ printout) \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)-usually 50mL (0.050L)
V = volume of sample digested (L)
DF = dilution factor

11.1.2 The Reporting Limit (RL) of the target analyte in liquid samples is calculated as follows:

$$Concentration(mg/L) = RLqap \otimes \frac{F}{V} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
RLqap = reporting limit from STL LQM (ug/L)
F = final volume of the sample digestate (L)
V= volume of sample digested (L)
DF = dilution factor

The LQM Reporting Limits assumes:
F = 50mL, V = 50mL, and DF = 1

11.2 Soil/Solid Samples

Soils and solids are routinely reported in mg/kg while the ICP is routinely calibrated in ug/L. If the results are reported in ug/kg, the conversion factor is omitted from the calculation.

11.2.1 The concentration of the target analyte in soil and solid samples is calculated as follows:

$$Concentration(mg/kg, dw) = ug/L(from\ printout) \otimes \frac{F}{W \otimes solids} \otimes DF \otimes \frac{1mg}{1000ug}$$

where
F = final volume of the sample digestate (L)
W = volume of sample digested (kg)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)
(for example, if the percent solids is 85%, the decimal equivalent is 0.85; if the %solids is 100%, the decimal equivalent is 1.0.)

11.2.2 The Reporting Limit (RL) of the target analyte in soil/solid samples is calculated as follows:

$$Concentration(mg/kg, dw) = RL_{qap} \otimes \frac{0.0010kg}{W \otimes solids} \otimes \frac{F}{0.100L}\ x\ DF$$

where
RL(qap) = reporting limit from LQM
W = weight of sample digested (kg)
F = final volume of the sample digestate (L)
V = volume of sample digested (L)
DF = dilution factor
solids = decimal equivalent of the percent solids (percent solids/100)

The LQM Reporting Limits assumes F = 0.100L (100mL), DF = 1, W = 0.0010kg (1.0g), and solids = 1.0

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 STL SOP AN02: *Analytical Batching* and the SOP Summary provide guidance on evaluating QC and sample data, including recommended corrective actions.

12.2 The method detection limit (MDL) is determined annually in accordance with STL SOP CA90. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP.

12.3 Determination of the Instrument Detection Limit (IDL)

The difference between the MDL and the IDL is the *digestion step*. The MDL samples are prepared and digested prior to analysis. The IDL is defined as three times the standard deviation of seven replicate analyses analyzed over three non-consecutive days. The concentrations of the IDL and MDL solutions are given in Section 8 of this SOP. See SOP CA91 for the procedures for the determination of the IDL.

12.4 The linear range of the ICP must be determined at least annually. The procedure for the determination is given in Section 10.7 of this SOP. If any calibration regression fit, other than linear, is utilized for the calibration of the ICP (i.e., Curvilinear or Full Fit), the upper limit of the linear range is the concentration of the High Standard.

12.5 Interelement correction factors (IEC) for all elements must be determined annually. Use the manufacturer's guidance for determination of the IECs. The IECs must be verified at the beginning and end of each analytical sequence.

13.0 TROUBLESHOOTING AND PREVENTIVE MAINTENANCE

LABORATORY EQUIPMENT PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	**Service Interval**							**SERVICE LEVEL**
	D	**W**	**M**	**Q**	**SA**	**A**	**AN**	
ICAP								
Pump Tubing	X							Change.
Nebulizer							X	Clean.
Filters			X					Inspect monthly, clean or replace as needed.
Spray Chamber							X	Clean.
Quartz Torch							X	Clean and realign.

D = daily W = Weekly M = monthly Q = Quarterly SA = semi-annually A = annually AN = as needed

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, reagents, and digests must be disposed of in accordance with SOP CA70: *Waste Management*.

15.0 REFERENCES

15.1 *Methods for Chemical Analysis of Water and Waste*; U.S EPA Office of Research and Development: Cincinnati, OHIO, March 1983.

15.2 *Test Methods for Evaluating Solid Waste, Third Edition*; U.S. EPA Office of Solid Waste and Emergency Response: Washington, D.C., November 1986.

15.3 *Methods for the Determination of Metals in Environmental Samples*; US EPA Office of Research and Development. Washington, DC.

TABLE 1

Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Aluminum (Al)	308.215	10	1.0/5.0	0.20	800	2.0	200
Antimony (Sb)	206.838	10	1.0/0.50	0.020	10	0.50	50
Arsenic (As)	189.042 193.696	1.0	1.0/0.50	0.010	25	2.0	200
Barium (Ba)	493.409	10	1.0/5.0	0.010	10	2.0	200
Beryllium (Be)	313.042	1.0	1.0/0.50	0.0040	10	0.050	5.0
Boron (B)	249.678	10	1.0/5.0	0.050	100	1.0	100
Cadmium (Cd)	226.502 228.802	1.0	1.0/5.0	0.0050	10	0.050	5.0
Calcium (Ca)	317.933 315.887	10	1.0/5.0	0.50	800	5.0	500
Chromium (Cr)	267.716	10	1.0/5.0	0.010	25	0.20	20
Cobalt (Co)	228.616	1.0	1.0/0.50	0.010	25	0.50	50
Copper (Cu)	324.754	10	1.0/5.0	0.020	50	0.25	25
Iron (Fe)	259.940 271.441	10	1.0/5.0	0.050	800	1.0	100
Lead (Pb)	220.353	1.0	1.0/0.50	0.0050	5	0.50	50
Magnesium (Mg)	279.079	10	1.0/5.0	0.50	1000	5.0	500

TABLE 1

Element	Wavelength (nm)	Calibration Conc. (mg/L)	ICV/CCV Conc. (mg/L)	RL Std. Conc. (mg/L)	Linear Range Std. Conc. (mg/L)*	MATRIX SPIKE CONC. (mg/L)	
						Water (mg/L)	Soil (mg/kg)
Manganese (Mn)	257.610	10	1.0/5.0	0.010	50	0.50	50
Molybdenum (Mo)	202.030	1.0	1.0/0.50	0.010	50	0.50	50
Nickel (Ni)	231.604	5.0	1.0/2.5	0.040	10	0.50	50
Potassium (K)	766.491	20	10/5.0	1.0	50	5.0	500
Selenium (Se)	196.026	10	1.0/5.0	0.010	25	2.0	200
Silver (Ag)	328.068	1.0	1.0/5.0	0.010	5.0	0.050	5.0
Sodium (Na)	588.995 330.231	10	1.0/5.0	0.50	20	5.0	500
Strontium (Sr)	421.552	10	1.0/5.0	0.010	100	0.50	50
Thallium (Tl)	189.042 190.801 377.572	10	1.0/5.0	0.010	30	2.0	200
Tin (Sn)	189.989	10	1.0/5.0	0.050	50	1.0	100
Titanium (W)	334.941	10	1.0/5.0	0.010	10	1.0	100
Vanadium (V)	292.402	10	1.0/5.0	0.010	50	0.50	50
Zinc (Zn)	213.856 206.200+	5.0	1.0/2.5	0.020	20	0.50	50

*For guidance only-instrument sensitivity will vary.

APPENDIX A
SOP SUMMARY

METHOD SUMMARY - ICP ANALYSIS

HOLD/STORAGE

Container	Minimum 250mL plastic bottle with plastic or Teflon-lined lid
Preservative	HNO3 to pH <2 in the field. If dissolved metals are required, filter the samples before preservation.
Storage	Liquids preserved to pH <2 may be stored at room temperature until preparation. Solid samples must be stored at 4C (less than 6C but not frozen) until preparation.
Hold Time	Samples must be analyzed within six months from the time of collection.

SAMPLE PREPARATION

Samples should be prepared with the appropriate matrix-specific procedure.

ANALYTICAL SEQUENCE

Ignite Plasma	Follow instrument manufacturer's guidelines and allow instrument to stabilize for at least 60 minutes.
Profile Instrument	Follow manufacturer's guidelines.
Initial Calibration	Calibrate with a blank and a high standard or a blank and three standards. Verify calibration by reanalyzing highest concentration standard for each element.
Initial Calibration Verification (ICV/ICB)	Analyze an initial calibration verification solution at the beginning of the run. ICV solution must come from a source other than the calibration standard source. Analyze a calibration blank after the ICV.
Continuing Calibration Verification (CCV/CCB)	Analyze a standard with concentrations at or near mid-range levels of the calibration. The CCV should be analyzed every 10 samples and at the end of the analysis run Analyze a continuing calibration blank after every CCV.
Interference Check Solutions	At the beginning and the end of an analysis run, verify the inter-element and background corrections by analyzing the interferent check solutions (ICSA & ICSAB).
Detection limit check solution	At the beginning and the end of an analysis run and verify the accuracy at the RL by analyzing a solution at the SL RL
Serial Dilution	Perform serial dilution (1/5) on a representative sample from each batch..
Post Digestion Spike Recovery.	To check for possible matrix interference, analyze a post digestion spike on a representative sample (minimum of 1 per batch). The post-digestion spike is evaluated if the serial dilution fails or if the analyte concentration in the sample is not at least 50 times the instrument detection limit.

QC Item	Frequency	Criteria	Corrective Action
Initial Calibration	Daily	1 std. and 1 blank	
Initial Calibration: Multi-point-minimum 3 stds and 1 blank	Daily	Correlation ≥0.995	Recalibrate
Highest Standard	Immediately after every calibration	Recoveries within ± 5% of expected values	New initial calibration
Initial Calibration Verification Standard (ICV)	At the beginning of the analysis	SW846 = within ±10% 200.7 = within ± 5%	Recalibrate
Continuing Calibration Verification Standard (CCV)	At the beginning and end of the analysis, and every 10 samples	Within ±10% of the true value, 200.7-NPDES - within ± 5% 200.7-Drinking Water – within ±10%	Terminate the analysis, fix the problem and reanalyze the previous 10 samples.
Calibration Blank (ICB/CCB)	After ICV and every CCV	Absolute value of the calibration blank must be less that the RL/CRDL	Terminate the analysis, correct the problem and reanalyze the previous 10 samples
Interference check standards (ICSA/ICSAB)	At the beginning and end of an analysis run	Determined values must be within ± 20% of the true values. Pay attention to false positives and false negatives for elements not present in the solutions.	Terminate the analysis, correct the problem, recalibrate, and reanalyze all samples since the last ICS that was in control.
Lab control sample	One per batch of twenty samples or less	6010B: STL LQM 200.7: 85-115%	Redigest and reanalyze batch
Preparation blank - SW846	One per batch of twenty samples or less	|result| <RL or result <5% of the analyte level in the sample.	Redigest and reanalyze batch
Preparation blank - 200.7	One per batch of twenty samples or less	|result| <RL or result <10% of the analyte level in the sample	Redigest and reanalyze batch
MS/MSD - SW846	One set per batch of twenty samples or less	STL LQM	Flag and report data
Serial Dilution (1/5 Dilution)	One per batch of twenty samples or less	See section 10.3.4	
Post Digestion Spike	One per batch of twenty samples or less	See section 10.4.5	
Detection Limit Check Solution	At the beginning and end of an analysis run	Recovery +/-50% of the true concentration.	Stop the analysis, fix the problem and reanalyze the affected samples.

APPENDIX B
EXAMPLES OF STANDARD PREPARATION

GENERAL INSTRUCTIONS
All calibration standards must contain 5% hydrochloric acid and 1% nitric acid by volume. The following table lists the volume of each acid needed to prepare the desired final volume of standard.

Final Volume of Standard (mL)	Volume of Hydrochloric acid (mL)	Volume of Nitric Acid (mL)
100	5.0	1.0
200	10	2.0
500	25	5.0
1000	50	10

For example, to prepare 500mL of a standard:

- Add 100mL to 200mL of reagent water to a clean 500mL volumetric flask.
- Add 5.0mL of concentrated nitric acid (HNO_3) and 25mL of hydrochloric acid (HCl) to the volumetric flask.
- Add the volumes of the stock standards given in the table to the volumetric flask:
- Dilute to a final volume of 500mL with reagent water. Store the standard at room temperature.

SINGLE POINT CALIBRATION STANDARDS FOR 6010

Calibration Standard 1-Calibration Blank (ICB, CCB)

Add 500mL to 600mL of reagent water to a clean 1-L volumetric flask. Add 10mL of concentrated nitric acid (HNO_3) and 50mL of hydrochloric acid (HCl) to the volumetric flask. Dilute to a final volume of 1.0-L with reagent water. Store the standard at room temperature. Other volumes may be prepared at the discretion of the lab. The nitric acid concentration must be 1% by volume and the hydrochloric acid concentration must be 5% by volume.

Calibration STANDARD 2

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (ml)	Conc. of Cal Std (mg/L)
Silver(Ag)	1000	0.50	500	1.0
Arsenic(As)	1000	0.50		1.0
Molybdenum(Mo)	1000	0.50		1.0
Lead(Pb)	1000	0.50		1.0
Selenium(Se)	1000	5.0		10
Antimony(Sb)	1000	0.50		1.0
Thallium(Tl)	1000	5.0		10

Calibration STANDARD 3

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Beryllium(Be)	1000	0.50	500	1.0
Barium(Ba)	1000	5.0		10
Cadmium(Cd)	1000	0.50		1.0
Cobalt(Co)	1000	0.50		1.0
Chromium(Cr)	1000	5.0		10
Copper(Cu)	1000	5.0		10
Manganese(Mn)	1000	5.0		10
Nickel(Ni)	1000	2.5		5.0
Zinc(Zn)	1000	2.5		5.0

Calibration STANDARD 4

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum(Al)	10000	0.50	500	10
Iron(Fe)	10000	0.50		10
Boron(B)	1000	5.0		10
Strontium(Sr)	1000	5.0		10
Titanium (Ti)	1000	5.0		10

Calibration STANDARD 5

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Calcium(Ca)	10000	0.50	500	10
Potassium(K)	10000	1.0		20
Magnesium(Mg)	10000	0.50		10
Sodium(Na)	10000	0.50		10
Tin(Sn)	1000	5.0		10
Vanadium(V)	1000	5.0		10

MULTI-POINT INSTRUMENT CALIBRATION-200.7

For all drinking water samples (EPA 200.7) the ICP must be calibrated with a minimum of three standards and a blank. The following standards may be used for this purpose. With the Thermo Jarrell Ash software the Calibration Analysis and Curve-fit programs must be used to be successful with the multi-point calibration of the ICP instruments.

High Standard.

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of Cal Std (mg/L)
Aluminum (Al)	10000	1.0	1000	10
Antimony (Sb)	1000	1.0		1.0
Arsenic (As)	1000	1.0		1.0
Boron (B)	1000	10		10
Barium (Ba)	1000	10		10
Beryllium (Be)	1000	1.0		1.0
Cadmium (Cd)	1000	1.0		1.0
Calcium (Ca)	10000	1.0		10
Cobalt (Co)	1000	1.0		1.0
Chromium (Cr)	1000	10		10
Copper (Cu)	1000	10		10
Iron (Fe)	10000	1.0		10
Lead (Pb)	1000	1.0		10
Magnesium (Mg)	10000	1.0		10
Manganese (Mn)	1000	10		10
Molybdenum Mo)	1000	1.0		1.0
Nickel (Ni)	1000	5.0		5.0
Potassium (K)	10000	1.0		10
Selenium (Se)	1000	10		10
Silver (Ag)	1000	1.0		1.0
Sodium (Na)	10000	1.0		10
Strontium (Sr)	1000	10		10
Thallium (Tl)	1000	10		10
Tin (Sn)	1000	10		10
Titanium (Ti)	1000	10		10
Vanadium (V)	1000	10		10
Zinc (Zn)	1000	5.0		5.0

Mid-Level Standard- Prepare as the CCV is prepared.

Low-Level Standard- Prepare as the RL/PQL Check Standard.

Initial Calibration Verification (ICV) Solution

Element/Stock	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
SPEX QC19	(1)	5.0	500	(2)
SPEX QC 7	(1)	5.0		(2)
Tin(Sn)	1000	0.50		1.0
Strontium (Sr)	1000	0.50		1.0
Potassium (K)	10000	0.50		10(3)
Sodium (Na)	10000	0.45		10(3)

(1) SPEX QC19 and SPEX QC7 are solutions containing multiple elements. The concentrations are given on the certificate of analysis.

(2) The final concentrations of the various elements are the same as listed in Table 1. The SPEC QC solutions are diluted by a factor of 100 from the concentration listed on the certificate of analysis.

(3) These concentrations include the contribution from SPEX Solutions QC-7

Continuing Calibration Verification (CCV) Standard

(also used as midpoint of multi-point calibration for EPA 200.7)

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. of CCV Std (mg/L)
Aluminum (Al)	10000	0.50	1000	5.0
Antimony (Sb)	1000	0.50		0.50
Arsenic (As)	1000	0.50		050
Boron (B)	1000	5.0		5.0
Barium (Ba)	1000	5.0		5.0
Beryllium (Be)	1000	0.50		0.50
Cadmium (Cd)	1000	0.50		0.50
Calcium (Ca)	10000	0.50		5.0
Cobalt (Co)	1000	0.50		0.50
Chromium (Cr)	1000	5.0		5.0
Copper (Cu)	1000	5.0		5.0
Iron (Fe)	10000	0.50		5.0
Lead (Pb)	1000	0.50		0.50
Magnesium (Mg)	10000	0.50		5.0
Manganese (Mn)	1000	5.0		5.0
Molybdenum (Mo)	1000	0.50		0.50
Nickel (Ni)	1000	2.5		2.5
Potassium (K)	10000	0.50		5.0
Selenium (Se)	1000	5.0		5.0
Silver (Ag)	1000	0.50		0.50
Sodium (Na)	10000	0.50		5.0
Strontium (Sr)	1000	5.0		5.0
Thallium (Tl)	1000	5.0		5.0
Tin (Sn)	1000	5.0		5.0
Titanium (Ti)	1000	5.0		5.0
Vanadium (V)	1000	5.0		5.0
Zinc (Zn)	1000	2.5		2.5

Reporting Limit (RL) Check Standard

(also used as low point in multi-point calibrations; e.g. EPA 200.7)

Preparation of RL/PQL Stock A-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Silver (Ag)	1000	0.10	100	1.0
Arsenic (As)	1000	0.10		1.0
Cadmium (Cd)	1000	0.050		0.50
Copper (Cu)	1000	0.20		2.0
Nickel (Ni)	1000	0.40		4.0
Lead (Pb)	1000	0.050		0.50
Selenium (Se)	1000	0.10		1.0
Thallium (Tl)	1000	0.10		1.0

Preparation of RL/PQL Stock B-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume (mL)	Conc. Of Stock Std (mg/L)
Aluminum (Al)	10000	0.20	100	20
Boron (B)	1000	0.50		5.0
Barium (Ba)	1000	0.10		1.0
Beryllium (Be)	1000	0.040		0.40
Calcium (Ca)	10000	0.50		50
Cobalt (Co)	1000	0.10		1.0
Chromium (Cr)	1000	0.10		1.0
Iron (Fe)	10000	0.050		5.0
Magnesium (Mg)	10000	0.50		50
Manganese (Mn)	1000	0.10		1.0
Molybdenum Mo)	1000	0.10		1.0
Sodium (Na)	10000	0.50		50
Antimony (Sb)	1000	0.20		2.0
Strontium (Sr)	1000	0.10		1.0
Tin (Sn)	1000	0.50		5.0
Titanium (Ti)	1000	0.10		1.0
Vanadium (V)	1000	0.10		1.0
Zinc (Zn)	1000	0.20		2.0

Preparation of RL/PQL Stock C-ICP

Element	Conc. of Stock Std	mL of Stock Std	Final Volume of Cal Std	Conc. Of Stock Std
Potassium(K)	10000	1.0	100	100

Preparation of the RL/PQL Check Solution-ICP

RL/PQL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A-ICP	5.0	500
Stock B-ICP	5.0	
Stock C-ICP	5.0	

ICP Interference Check Solutions

Preparation of ICP Interference Check Solution A

Element	Conc. Of Stock(mg/L)	mL of Stock Std	Final Volume(mL)	Conc. (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200

Preparation of ICP Interference Check Solution AB

Element	Conc. of Stock(mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std (mg/L)
Aluminum (Al)	10000	25	500	500
Calcium (Ca)	10000	25		500
Magnesium (Mg)	10000	25		500
Iron (Fe)	10000	10		200
Silver (Ag)	1000	0.10		0.20
Arsenic (As)	1000	0.050		0.10
Barium (Ba)	1000	0.25		0.50
Beryllium (Be)	1000	0.25		0.50
Cadmium (Cd)	1000	0.50		1.0
Cobalt (Co)	1000	0.25		0.50
Chromium (Cr)	1000	0.25		0.50
Copper (Cu)	1000	0.25		0.50
Manganese (Mn)	1000	0.25		0.50
Nickel (Ni)	1000	0.50		1.0
Lead (Pb)	1000	0.025		0.050
Antimony (Sb)	1000	0.30		0.60
Selenium (Se)	1000	0.025		0.050
Thallium (Tl)	1000	0.050		0.10
Vanadium (V)	1000	0.25		0.50
Zinc (Zn)	1000	0.50		1.0
Molybdenum (Mo)	1000	0.50		1.0
Tin (Sn)	1000	0.50		1.0

ICP Matrix Spiking Solutions

ICP Matrix Spiking Solution 1 is a solution purchased from SPEX. The certificate of analysis will list the concentrations of the analytes. Store this solution at room temperature. Prepare this solution every six months or sooner if needed or required.

Preparation of the ICP Matrix Spiking Solution 2

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron (B)	1000	10	100	100
Calcium (Ca)	10000	5.0		500
Magnesium (Mg)	10000	5.0		500
Molybdenum (Mo)	1000	5.0		50
Potassium (K)	10000	5.0		500
Sodium (Na)	10000	5.0		500
Strontium (Sr)	1000	5.0		50
Tin (Sn)	1000	10		100
Titanium (Ti)	1000	10		100

IDL/MDL Solution

The IDL/MDL solution is used in this procedure for two purposes:

1) To determine the Instrument Detection Limit (IDL) of each target compound on a quarterly basis (SOP CA91); and
2) To determine the Method Detection Limit (MDL) of each target compound on an annual basis (SOP CA90). MDLs should be digested straight and at 1:2 dilutions.

Preparation of IDL/MDL Stock A

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Silver (Ag)	1000	0.040	100	0.40
Arsenic (As)	1000	0.20		2.0
Barium (Ba)	1000	0.020		0.20
Beryllium (Be)	100	0.050		0.050
Cadmium (Cd)	1000	0.040		0.40
Lead (Pb)	1000	0.10		1.0
Antimony (Sb)	1000	0.20		2.0
Selenium (Se)	1000	0.20		2.0
Thallium (Tl)	1000	0.20		2.0

Preparation of IDL/MDL Stock B

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. Of Std. (mg/L)
Cobalt (Co)	1000	0.030	100	0.30
Chromium (Cr)	1000	0.10		1.0
Copper (Cu)	1000	0.10		1.0
Manganese (Mn)	1000	0.020		0.20
Molybdenum (Mo)	1000	0.040		0.40
Nickel (Ni)	1000	0.10		1.0
Tin (Sn)	1000	0.20		2.0
Vanadium (V)	1000	0.060		0.60
Zinc (Zn)	1000	0.10		1.0

Preparation of IDL/MDL Stock C

Element	Conc. of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Aluminum (Al)	10000	0.10	100	10
Calcium (Ca)	10000	0.10		10
Iron (Fe)	10000	0.10		10
Magnesium (Mg)	10000	0.10		10
Potassium (K)	10000	0.20		20
Sodium (Na)	10000	0.040		4.0

IDL/MDL Solution

Preparation of IDL/MDL Stock D

Element	Conc. Of Stock (mg/L)	mL of Stock	Final Volume (mL)	Conc. of Std. (mg/L)
Boron(B)	1000	0.40	100	4.0
Strontium (Sr)	1000	0.040		0.40
Titanium (Ti)	1000	0.050		0.50
Sodium (Na)	10000	2.0		200

Preparation of the IDL/MDL Check Solution

IDL/MDL Stock	mL of RL/PQL Stock	Final Volume(mL)
Stock A	5.0	1000
Stock B	5.0	
Stock C	5.0	
Stock D	5.0	

The IDL/MDL Check Solution contains the following elements at the given concentrations:

Element	Concentration(mg/L)
Be	0.00025
Ba, Mn	0.0010
Co	0.0015
Ag, Cd, Mo, Sr	0.0020
Ti	0.0025
V	0.0030
Cr, Cu, Ni, Pb, Zn	0.0050
As, Sb, Se, Sn, Tl	0.010
Na(1), B	0.020
Ca, Fe, Mg	0.050
Al, K	0.10
Na	1.0

(1) If the wavelength for sodium is 588.995, the lower concentration (0.020mg/L) is used for the IDL./MDL check solution. In this case, only stocks A,B, and C are used to make the IDL/MDL Check Solution. IDL/MDL Check Solutions for B, Sr, and Ti are prepared and evaluated separately.

Approval Signature: R. Wayne Robbins	
Title: Corporate QA Manager	Date: July 6, 1998

WASTE DILUTION EXTRACTION

1.0 SCOPE AND APPLICATION

The procedures in this SOP can be used to extract semi-volatile organic compounds from matrices such as oils and organic wastes that are soluble in the extraction solvent. The following parameters may be determined using this procedure:

PARAMETERS	EPA METHOD/SL SOP	DILUTION SOLVENT
Pesticides and PCBs	8081/8082 (SG45)	Hexane
PCBs	8082(SG45)	Hexane
Base/Neutrals/Acids	8270(SM05)	Methylene chloride
Petroleum products	8015-extractables(SG70)	Methylene chloride

The waste dilution procedure for chlorinated herbicides is given in SL SOP EX45.

2.0 SUMMARY OF METHOD

2.1 A 0.2g to 1g aliquot of the sample is diluted in an appropriate solvent. The extract is filtered to remove any particulates and analyzed by the appropriate analytical procedure.

For BNA by 8270, petroleum products by 8015-ext, and pesticides by 8080/8081, the sample is diluted without the addition of surrogates and the LCS and MS are not required. Generally, waste dilutions for these parameters will require additional dilution beyond the initial waste dilution. This additional dilution results in the surrogates and matrix spikes falling below the lowest level of the calibration curve; therefore surrogates are not added nor are martix spikes or lab spikes required for waste dilutions for when .

2.2 This procedure is based on SW-846 Method 3580A.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedure that you do not understand or that will put you or others in potentially hazardous situations.

3.2 The analyst must wear a lab coat or apron, eye protection, and gloves when performing any part of this procedure. The extract cleanup must be performed under a hood or in a well ventilated area. The acid and permanganate cleanups include the use of a strong acid (sulfuric acid) and a strong oxidizer (potassium permanganate). These chemicals will burn unprotected skin and destroy unprotected clothing.

3.3 Material Safety Data Sheets (MSDS) are available for reference at each lab division. The analyst should be familiar with the potential hazard that each reagent poses and the procedures for safely handling the material.

4.0 INTERFERENCES

Non-target compounds co-extracted from the sample matrix may interfere with the extraction, cleanup, or GC analysis. If the acid, permanganate, and sulfur cleanup does not result in a clean extract, the recommended course of action is to dilute the extract or to start over with a smaller aliquot.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Oil and wastes are routinely collected in glass containers equipped with Teflon-lined caps. The samples are stored at room temperature. The sample should be extracted within 14 days of collection and the extract should be analyzed within 40 days of extraction.

6.0 MATERIALS AND APPARATUS

6.1 12mL vials equipped with Teflon-lined caps

6.2 Disposable Pasteur pipettes

6.3 Volumetric flasks - class A, various volumes

6.4 Top-loading balance - capable of weighing to 0.01g

7.0 REAGENTS

7.1 Hexane - residue grade or better

7.2 Methylene chloride - residue grade or better

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with SL SOP AN41:*Standard Material Traceability*. General guidance on the preparation of standards is given in SL SOP AN43:*Standard Preparation.*

The lab should purchase certified solutions from SL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SL SOP AN43 for guidance for standard preparation.

8.1 Determine the volume of standard to be prepared and the volume of the stock standard needed to make the spiking standard. The following equation can be used:

$$Cstock \otimes Vstock = Cspike \otimes Vspike$$

$$Vstock = \frac{Cspike \otimes Vspike}{Cstock}$$

where
Vstock = volume of stock standard (or *initial standard*) needed to prepare the spiking solution(mL)
Cstock = concentration of stock solution(or *initial standard*)(ug/mL)
Ccal = concentration of calibration standard to prepare(*final concentration*)(ug/mL)
Vcal = volume of calibration standard to prepare(*final volume*)(mL)

The concentration can be expressed in whatever terms the analyst finds most convenient - ug/L, ug/mL, mg/L, etc. The units must be the same for *Cstock* and *Ccal.*

In some instances, the stock solution is used as the spiking solution.

8.2 PCBs

8.2.1 Pesticide and PCB Surrogate spiking solution - Add 100ul of the Pesticide Surrogate standard (Restek P/N 320000 200ug/ml) to a 1.0ml volumetric flask containing about 0.5ml of hexane. Dilute to volume and mix thoroughly. The spiking solution has a concentration of 20ug/ml. (TCMX and DCB).

8.2.2 PCB Matrix Spiking Solutions

Ar1016	Restek P/N 32006	1000ug/ml
Ar1260	Restek P/N 32012	1000ug/ml

These solutions are spiked directly into the LCS and MS/MSD.

9.0 SAMPLE PREPARATION

9.1 General Sample Preparation Instructions

The waste dilution procedure is an efficient means of getting soluble materials into a solvent that can be analyzed by gas chromatography. A small aliquot of sample, usually 1g, is transferred to a glass vial and diluted in a solvent that is compatible with the analytical system. For example, don't use methylene chloride for pesticides and PCBs since the electron capture detector is extremely sensitive to chlorinated compounds. The table in section1 lists the solvents that are routinely used for the various analyses.

The analyst must be aware that the waste dilution may contain high concentrations of target and non-target compounds. Samples with non-volatile materials (e.g., heavy oils) can adversely affect the detection of the target compounds in subsequent analyses as non-volatile materials are deposited in the injection port and become a source of "active sites". In general, it is recommended to dilute the sample 1:10 or 1:100 for the analysis and analyze more concentrated extract aliquots as the sample is characterized.

9.2 PCBs in Wastes and Oils
The extract is subjected to the cleanup steps listed in SL SOP EX60.

9.2.1 Weigh 1.0g of the oil into a glass container and dilute to 10.0mL with hexane. For a waste oil or oil with debris or sludge, weigh 0.20g into a vial. Record the weights to the nearest 0.01g. Weigh two additional aliquots of one sample in the batch for the MS and MSD.

The glass vial should be equipped with a cap that is resistant to acids and strong oxidizers. The vials used for volatiles are suitable since they have Teflon-lined caps. Mark the volume on the side of the container.

NOTE: It is important to maintain a constant volume of hexane throughout the extraction, cleanup, and analysis procedures.

9.2.2 Add 10.0mL of hexane to each of two glass vials. Label one as the method blank and the other as the LCS. Dilute each sample to a final volume of 10mL.

NOTE: A method blank, LCS, MS, and MSD must be extracted and analyzed with each batch of twenty or fewer samples. If a cleanup is employed, all QC items must be subjected to the cleanup.

9.2.3 Add 10uL (10 microliters) of the pesticide surrogate spiking solution (20ug/mL) to each sample, blank, LCS, and MS/MSD. The theoretical concentration is

If 1g is extracted:

$$surrogate\ (mg/kg) = \frac{0.010mL\ x\ 20ug/mL}{0.0010kg} = 200ug/kg = 0.20mg/kg$$

$$surrogate\ (mg/kg) = \frac{0.010mL\ x\ 20ug/mL}{0.0002kg} = 1000ug/kg = 1.0mg/kg$$

If 0.20g is extracted:

9.2.4 Add 10uL (10 microliters) of the AR1016 stock solution (1000ug/mL) and 10uL of the AR1260 stock solution(1000ug/mL) to the LCS and MS/MSD. The theoretical concentration of each Aroclor is

If 1.0g is extracted:

$$LCS\ /\ MS\ (mg/kg) = \frac{0.010mL\ x\ 1000ug/mL}{0.0010kg} = 10000ug/kg = 10mg/kg$$

If 0.20g is extracted:

$$MS\ (mg/kg) = \frac{0.010mL\ x\ 1000ug/mL}{0.00020kg} = 10000ug/kg = 50mg/kg$$

Assume that the weights of the method blank and LCS are 1.0g.

NOTE: PCBs-The surrogates and spikes must be added to the samples in such a way to minimize the volume of water-soluble solvents such as acetone. The water-soluble solvents may partition into the acid or oxidizer during the cleanup steps, reducing the total volume of solvent and making the recoveries and results high biased.

10.0 PROCEDURE

The analytical determinations are given in the referenced SL SOPs. See table in section 1.

11.0 DATA ANALYSIS AND CALCULATIONS

The analytical determinations are given in the referenced SL SOPs. See table in section 1.

12.0 QUALITY ASSURANCE/QUALITY CONTROL

The analytical batch for PCBs consists of twenty field samples and the following QC items: method blank and LCS. MS and MSD are prepared and analyzed at a frequency of 5% of samples or as requested. The evaluation of batch QC data is given in SL-SOP AN02: *Analytical Batching*. Surrogate recoveries and spike recoveries are evaluated using the waste limits listed in the CQAP, Table 5.7.

Samples for the BNA, pesticides, and petroleum products are diluted in the appropriate solvent. A solvent blank is analyzed for each batch of samples.

13.0 PREVENTIVE MAINTENANCE

No items in this revision

14.0 TROUBLESHOOTING

No items in this revision

15.0 REFERENCES

15.1 *Savannah Laboratories' Comprehensive Quality Assurance Plan* and *Savannah Laboratories' Corporate Quality Assurance Plan*, current revisions.

15.2 *Test Methods for Evaluating Solid Waste*, Third Edition, SW-846, US EPA Office of Solid Waste and Emergency Response: Washington, DC.

SEVERN TRENT SERVICES

ORGANOCHLORINE PESTICIDES AND PCBs BY GC
(Methods 608, 8081A, and 8082)

Approved by: R. Wayne Robbins 30 January 2002
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures used to determine the concentration of chlorinated pesticides and polychlorinated biphenyls (PCBs) as Aroclors in various matrices. Appendix A contains an example of the retention time order for the single peak pesticides, Appendix B provides examples of the calibration standards routinely analyzed, and Appendix C contains a summary of the method QC requirements for Methods 608, 8081A, and 8082.

1.2 The routine target compounds, reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria are listed in Section 5 of the current revision of the laboratory quality manual (LQM) for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Environmental samples are prepared using matrix-specific procedures (see Section 9). The solvent is evaporated, the residue exchanged into hexane, and the sample adjusted to a final volume of 10mL or less. The preparation may also incorporate Florisil, copper (sulfur), acid (PCBs and Toxaphene only), or gel permeation chromatography (GPC) cleanups. Analysis of the extract is routinely performed on a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. GC/MS confirmation can also be employed if analyte concentration is sufficiently high or if the sample extract is concentrated to an appropriate final volume. Quantitation may be performed using the external or internal standards calibration technique.

2.2 Method Clarifications/Default Procedures

General Clarification: The procedures for chlorinated pesticides (8081A) and PCBs (8082) are given as separate methods in Update III of SW-846. In previous updates, pesticides and PCBs were included in a single method; pesticides and PCBs are still included in the scope of EPA Method 608. The extraction and the analysis are combined in this SOP 1) to reduce the time of extraction and analysis; and 2) to reduce the amount of solvent used in the procedures (one extraction instead of two). If interferences or high levels of non-PCB compounds are present, a portion of the extract will be subjected to the acid cleanup and reanalyzed. Note that if the list of target analytes includes only a limited list of components (i.e. Toxaphene, Chlordane, or PCBs), these procedures may be abbreviated to address only the analytes of interest.

Elimination of Calibration Points: When more calibration standards are analyzed than required, individual compounds may be eliminated from the lowest or highest concentration level(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of a calibration be eliminated without eliminating the entire level.

Bracketing Sample Extracts: The default procedure for continuing calibration verification is to bracket samples by CCV standards (before and after) if external standard calibration is used and ***not*** to cap the sequence (run CCV after the samples) if internal standard calibration is used ***unless*** noted in an agency or client QAPP or in an STL pre-project plan. The internal standard provides verification information on the sensitivity and retention time stability of the instrument and verification of acceptable injections of the sample extracts. See Appendix C for summaries of the analytical sequences.

Grand Mean: The "grand mean" is used to evaluate calibration data according to the provisions of SW-846 Method 8000B and Sections 10.3 and 10.4 of this SOP.

Quantitation of QC Items: The default procedure for the analysis and evaluation of QC items (method blank, LCS, and MS/MSD) is to analyze these items on one of the instruments used to analyze the associated samples. The default procedure is to quantify the QC items by the internal standard procedure if both internal and external calibration are used to quantify the associated samples.

Dilutions: Unless otherwise specified by a client or QA plan, results from a single dilution are reportable as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client.

For clients who demand lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 the dilution factor with the highest target in the upper half of the calibration curve. For example, a sample analyzed at a DF of 50 resulting in a hit in the upper half of the calibration curve would be reanalyzed at a DF of 5 to provide lower detection limits to the client. Project managers and lab staff must work together to balance client satisfaction with productivity.

2.3 This method is based on the guidance in SW-846 Methods 8000B, 8081A, and 8082 and 40 CFR 136 Method 608.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially hazardous situations.

3.2 The analyst should wear an apron or lab coat, gloves, and eye protection when handling extracts. Dilutions should be performed under a hood or in a well-ventilated area.

3.3 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in the analysis of pesticides and PCBs. Many of these compounds are suspected carcinogens.

4.0 INTERFERENCES

4.1 Glassware should be scrupulously cleaned and solvent-rinsed in accordance with STL SOP AN60 to minimize artifacts and/or elevated baselines in gas chromatograms. Any vessel that comes in contact with the extract is a potential source for contamination. Method blanks that are extracted and analyzed with each batch of samples will provide clues to the source of contamination from the glassware and reagents.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. See Section 9 for a table summary of the cleanups that may be employed to eliminate or reduce interferences. If matrix interferences continue after a cleanup has been performed, the sample is diluted as needed for data analysis. If a cleanup is used, the method blank must also be subjected to the cleanup.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Aqueous samples are collected in 1-L glass containers with Teflon-lined caps. Soil/sediment samples are collected in wide mouth glass jars equipped with Teflon lined caps. No preservative is added. The samples are iced at the time of collection and maintained at 4°C (less than 6C with no frozen samples) until extraction. Extraction must be performed within 7 days for aqueous samples and within 14 days of sampling for soils/solids. The extracts must be stored at 4°C (less than 6C) and must be analyzed within 40 days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph (GC), temperature programmable, equipped with single or dual electron capture (EC) detectors and a compatible autosampler

6.2 Data system compatible with the GC, with appropriate software or integration capabilities

6.3 The following column pairs are recommended. Other columns/phases may be used if the calibration and QC criteria are met and adequate separation of the target compounds is achieved.

DB-5 fused silica capillary column 30 M x 0.53 mm ID x 1.5 um film (J&W or equivalent)
DB-608 fused silica capillary column 30 M x 0.53 mm ID x 0.83 um film (J&W or equivalent)
<Or>
DB-5 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
DB-17 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
<Or>
DB-5 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)
DB-1701 fused silica capillary column 30 M x 0.32 mm ID x 0.5 um film (J&W or equivalent)

6.4 Microsyringes, appropriate volumes

6.5 Volumetric flasks, Class A, appropriate volumes

6.6 Autosampler vials, septa, and caps - compatible with the autosampler

7.0 REAGENTS

Hexane- pesticide grade, for preparation of standards

8.0 STANDARDS

The preparation of the calibration standards must be tracked in accordance with STL SOP AN41:*Standard Material Traceability*. General guidance on the preparation of standards is given in STL SOP AN43:*Standard Preparation*.

The lab should purchase certified solutions from STL approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See STL SOP AN43 for guidance for standard preparation.

Calibration Standard Recipes

The recipes used for standard preparation must be clearly documented as a controlled posting or as a narrative in the traceability log. The lowest level calibration standard should be at or below the equivalent of the reporting limit as defined in the LQM or client QAPP. The remaining standards will define the working range of the analytical system. Appendix B contains example recipes of the calibration levels for the routinely determined single peak pesticides, technical chlordane, toxaphene, and the Aroclors.

If internal standard calibration is used, each calibration standard must contain the same concentration of the internal standard(s). The recommended concentration range for the internal standard(s) is 0.050 to 0.10ug/mL.

9.0 SAMPLE PREPARATION

The sample preparation and cleanup procedures are described in the following SOPs:

PROCEDURE	MATRIX	STL SOP
Continuous Liquid-liquid extraction	aqueous and leachates	EX30
Separatory funnel extraction	aqueous and leachates	EX35
Ultrasonic extraction	soils and sediments	EX40
Waste dilution	Waste samples (oils, products, etc)	EX42
Zymark extract concentration	All extracts	EX50

CLEAN-UP PROCEDURE	STL SOP	APPLICATION	EFFECTIVENESS
Florisil	EX62	Pest/PCBs	Eliminates polar non-target compounds
Sulfuric acid / permanganate	EX60	PCBs and Toxaphene	Eliminates some unsaturated hydrocarbon interferences
Copper	EX60	Pest/PCBs	Eliminates elemental sulfur
GPC	EX61	Pest/PCBs	Eliminates high molecular weight non-target compounds and sulfur

10.0 ANALYTICAL PROCEDURE

10.1 Gas Chromatograph Operating Conditions

The instrument conditions listed in this section are for guidance. The actual conditions used by the lab must be documented in the instrument maintenance log, data system, or run log. The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

10.1.1 Two configurations are routinely used for the analysis of pesticides and PCBs. A single column may be connected to the injection port or two columns may be connected to the injection port using a press-tight glass y-splitter and a guard column, a two-hole ferrule, or a glass tee to provide simultaneous detection and confirmation of the target analytes.

10.1.2 Example GC Parameters

Injector: 220 – 240°C
Detector: 300 – 320 °C
Carrier Gas Flow: Helium at 5 mL/min (per column)
Make-up Gas Flow: Nitrogen at 25 mL/min (per detector)-see manufacturer's recommended flows

Example chromatogram temperature program:

Initial Temp:	160 C
Initial Hold:	4.0 min
Program Rate:	10 C/min
Final Temp:	270 C (hold for 10 minutes)
Injected Volume:	2-4uL - 1-2uL per column (single injection into guard column and "Y" splitter)

NOTE: These conditions and parameters are given for guidance. The columns/phases, GC conditions, and instrument parameters may be modified to optimize the analytical system.

10.2 Column Evaluation (608 and 8081A)

The column(s) must be evaluated prior to the analysis of the calibration standards and once every 12 hours. The column evaluation is performed by injecting Endrin and p,p'-DDT and calculating the percent breakdown of these compounds. The standard used for determining the percent breakdown must not contain any compounds that coelute with Endrin, DDT, or any of the corresponding breakdown products.

NOTE: The column evaluation does not have to be performed if PCBs only are the target compounds. PCBs are stable and not subject to breakdown in the injection port.

If the instrument has not been in use for more than one day, a "priming" analysis may be beneficial. The analysis of a relatively high concentration pesticide or PCB standard may help to stabilize the response of the very sensitive EC detector. Inject a standard that is about 10x the concentration of the highest calibration standard and allow the instrument to cycle through the temperature program. It is not necessary to acquire the data but the baseline should be monitored before and after the priming analysis to gauge the condition of the detector. A hexane blank should be analyzed after the analysis of the priming standard and before the %breakdown check.

NOTE: The "priming" standard should be injected manually to avoid contaminating the autosampler syringe.

Inject the Endrin/DDT breakdown standard. Check the peak integrations and calculate the breakdown as follows:

$$\%\text{Breakdown Endrin} = \frac{\text{Response(Endrin Aldehyde} + \text{Endrin Ketone)}}{\text{Response(Endrin} + \text{Endrin aldehyde} + \text{Endrin Ketone)}} \otimes 100$$

$$\%\text{Breakdown DDT} = \frac{\text{Response(DDE} + \text{DDD)}}{\text{Response(DDT} + \text{DDE} + \text{DDD)}} \otimes 100$$

The response (area or height) must be used to evaluate the breakdown. Do not use concentrations and do not "undetect" peaks that are below the RL or MDL. All peaks detected by the data system must be included in the percent breakdown calculation.

Breakdown Criterion

The breakdown for each compound must be less than 15%. If the breakdown exceeds 15%, the instrument will require column and/or injector port maintenance. The maintenance may include but is not limited to replacing the septum, clipping the front of the column, and replacing the glass injector sleeve.

10.3 Initial Calibration

Internal or external standard calibration techniques may be employed for the determination of the concentration of pesticides and PCBs. Pentachloronitrobenzene (PCNB) or 2-Nitro-1-bromobenzene is recommended for use as internal standards. Other compounds may be used for internal standards.

Internal standard calibration should be used as the default. If matrix interferences preclude the use of internal calibration for a sample extract, two options should be considered:

1) dilute the extract or perform sample extract cleanup to minimize or eliminate the interference
2) use external standard calibration to quantify the target and surrogate compounds (if external standard calibration is used, all calibration requirements, including a capping standard, must be met-see Appendix C for the external standard sequence)

10.3.1 Prepare and analyze the calibration standards. Injector port and column maintenance should be performed on the instrument prior to the analysis of the initial calibration standards. Guidance for establishing the analytical sequence is given in the SOP Summary.

Note that the following offers two (2) options for calibration and quantitation – average CF or regression curve. Only one needs be chosen per analyte.

10.3.2 Evaluate the standard chromatograms. Some questions to ask at this point are:

>Is there contamination in the hexane blank? If so, has maintenance been performed on the instrument lately? Has the septum been changed? Is the column properly seated in the injector and detector ports?
>Did all of the standards inject properly? Are there peaks for each of the standards analyzed? Do the patterns look normal?
>Are the peaks symmetrical? Is there tailing or fronting?
>Are the areas of the peaks normal for the sensitivity setting being used?

Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

10.3.3 Evaluate the calibration curve in accordance with SOP AN67: *Evaluation of Calibration Curves.*

10.3.4 Initial Calibration Criteria:

600-series: If the relative standard deviation is less than 10% for the target compounds in the initial calibration, the calibration is considered linear through the origin and the average calibration factor may be used for quantitation.

8000-series: If the relative standard deviation is less than 20% for the target compounds in the initial calibration, the calibration is considered linear through the origin and the average calibration factor may be used for quantitation.

The preferred method of quantitation is the average response or calibration factor. If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve (Section 10.2.5). The "grand mean exception" described below should be applied to 8081A and 8082 initial calibrations only in extraordinary circumstances because of the difficulty of maintaining and providing documentation on an on-going basis.

8000-series ICAL grand mean exception:
If one or more compounds exceed the %RSD criteria, the average calibration factors can be used for quantitation if the average %RSD of ALL of the compounds (the grand mean) in the ICAL is less than or equal to 20%.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required since the lab has demonstrated that the lowest standard in the calibration curve (the equivalent of the RL) can be detected.

Regression Curve Option: A calibration curve is established for each analyte by plotting the concentration along the x-axis and the corresponding response along the y-axis. If the regression coefficient of the regression curve is greater than 0.99, the curve can be used to quantify samples. For 8000-series methods, a minimum of five points is required for a linear regression, six points for a second order curve, and seven or more for higher order fits. It is recommended to use only linear and quadratic (second order) curves for quantitation. See STL SOP AN67 for guidance on evaluation of calibration curves.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

10.4 Calibration Verification

Calibration is verified at the frequency given in the SOP Summary. If external standard calibration is used, the following criteria apply to calibration standards analyzed before and after samples. In situations where compounds fail criteria high and no positive hits for the compound(s) failing high are detected, these samples may be reported.

If internal standard calibration is used, the samples do not have to be bracketed (capped) by the analysis of a CCV standard unless specified by a regulatory agency or client QAPP.

10.4.1 Analyze a mid-level standard. The concentration of the verification standard should be varied periodically to evaluate the calibration curve in the lower and upper halves. Tabulate the area of the target analytes and calculate the response factors if using the average RF/CF option. If using the calibration curve option, calculation of the RF is unnecessary.

Calculate the percent drift or percent difference between the initial and continuing calibration in accordance with SOP AN67.

10.4.2 Continuing Calibration Verification Criteria

Response Criteria:

If the CCV criterion is not met, another CCV should be analyzed. Repeated failure may be a sign of instrument or standard degradation. If the calibration verification criteria cannot be met, a new initial calibration must be prepared, analyzed, and evaluated.

600-series: If the percent drift or percent difference is less than or equal to 15%, the initial calibration is verified and the average response factor or regression curve can be used for quantitation.

8000-series: If the percent drift or percent difference is less than or equal to 15%, the calibration curve is verified and the average response factor or regression curve can be used for quantitation.

8000-series CCAL grand mean exception:
If one or more compounds exceed the %drift or %difference criteria, the average calibration factor or regression curve from the initial calibration can be used for quantitation if the average %drift or average % difference of ALL of the compounds (the grand mean) in the CCV is less than or equal to 15%.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

All samples analyzed using external standard calibration must be bracketed by acceptable CCV. If the CCV standard analyzed after the samples fails to meet the acceptance criteria and the response of the mid point standard is *above* the criteria (that is the response of the analytical system has increased), samples which have no target compounds detected above the RL may be reported as <RL, since the compounds would have been detected if present. (SW-846 Method 8000B).

Retention Time Criteria
The retention time for the CCV must fall within the daily retention time window as defined in STL SOP AN66: *Determination of Retention Time Windows for Gas Chromatographic Analyses.*

Internal Standard Response Criteria
If internal standard calibration is used, the response of the internal standard(s) must be within –50% to +150% of the response in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the ISTD response will require re-calibration.

RL Standard
An optional standard at the reporting limit (RL) may be analyzed in the analytical sequence to verify sensitivity of the target compounds. All target compounds in the RL standard should be recovered at 50-150% of its true concentration and all peaks should be adequately resolved. If the RL standard recovers within the specified limits, samples with no target compounds detected may be reported as such (i.e., less than the RL) regardless of whether the associated CCV passed the acceptance criteria.

10.5 Sample Analysis Sequence

The analytical sequences for the 600- and 8000-series methods are given in the SOP Summary in Appendix C. The default is to exclude QC items (method blanks, LCS, and MS/MSD) in determining the maximum number of extracts in the clock. For 8081and 8082, more than 20 extracts (samples and QC) may be analyzed in a sequence, as long as the 12 hour time frame has not elapsed, but the number of samples (non-QC extracts) may not exceed 20. Note that some client and agency QAPPs may require that the QC items be counted as part of the twenty samples.

10.5.1 The sample extract is injected using the same injection volume used for the calibration standards. Extracts that are known to be relatively clean should be analyzed first. Extracts suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

If the internal standard calibration is used, the concentration(s) of the internal standard(s) must be the same in all calibration samples, field samples, and QC samples. A concentration of 0.050ug/mL to 0.10ug/mL (final extract concentration) is recommended.

10.5.2 If the concentration of target compounds exceeds the working range (defined by the highest standard in the initial calibration), the extract must be diluted in hexane and reanalyzed. A dilution should bring the area of the largest peak of interest into the upper half of the calibration curve. If the internal standard calibration is used, the concentration of the internal standard in the diluted extract must be the same as in the calibration standards.

NOTE: Unless otherwise specified by a client or QA plan, results from a single dilution are reportable as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client.

For clients who demand lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 the dilution factor with the highest target in the upper half of the calibration curve. For example, a sample analyzed at a DF of 50 resulting in a hit in the upper half of the calibration curve would be reanalyzed at a DF of 5 to provide lower detection limits to the client. Project managers and lab staff must work together to balance client satisfaction with productivity.

10.5.3 Occasionally, situations may arise where part of the chromatogram is obscured by large non-target peaks (such as phthalate esters, which elute in the same general retention time range as the pesticides and PCBs) or matrix interferences (short, wide, peaks that are not well resolved). In these situations, it is permitted to report a lower RL for the target compounds that are not affected by the non-target or matrix interference and perform a dilution only for the target compounds that are affected. This anomalous situation must be discussed with the project manager and section supervisor prior to reporting the results and noted in the case narrative or anomaly report. Again, project managers and lab staff must work together to balance client satisfaction with productivity.

10.6 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in STL SOP AN66: *Determination of Retention Time Windows and Evaluation of Retention Time Data Chromatographic Analyses*. If internal standard calibration is used, the determination of absolute retention time windows is not required. Relative retention times, as described in Section 11.1.4, are used to identify the target compounds.

11.0 DATA ANALYSIS/CALCULATIONS

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times); the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration; and the integration of the peaks. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data. STL SOP AN66: *Determination of Retention Time Windows and Evaluation of Retention Time Data for Chromatographic Analyses* provides additional guidance for the evaluation of chromatographic data. This guidance is summarized in the following sections.

Manual integrations must be documented in accordance with STL SOP AN65: *Manual Integrations*. Data systems should be adjusted to minimize operator intervention. All chromatographic peaks must be evaluated for overall peak shape and "reasonableness" of integration. Under no circumstances should manual integrations be used to change reasonable data system integrations in order to meet calibration or QC criteria.

The judgement and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. The analyst should ask:

- Is there previous data or current information about the sample that would aid in evaluating the data?
- Do the peaks look normal?
- Are peaks properly integrated?
- Are co-eluting peaks or matrix interferences present?
- Is the internal standard present at the correct retention time and response (-50% to150% of the response in the associated CCV)? Are the surrogates present at the expected RT or have they shifted?

11.1 Qualitative analysis

Identification of the surrogates and target compounds is based on retention time. The retention time (RT) windows calculated around the CCV retention times are used for the identification of the target compounds. The analyst should also note shifts in the retention times of the surrogate compounds or internal standard(s) to help gauge possible shifts in the RT of the target compounds. If, in the professional judgement of the analyst and supervisor, a peak within the retention time window can be reasonably excluded as a target, the result may be reported as a "non detect". This may only be done when the RT of the internal standard and surrogates are at their respective retention times and there is little or no evidence of matrix interferences. If there is doubt as to whether the peak can be excluded or not, the default procedure will be to report the peak as the target compound unless another technique (for example, GC/MS) is used to determine that the target compound is not present.

NOTE: It is important to note that the retention time window applies only to peaks that are within the calibration range of the curve. Peak areas that exceed the established linear range of the calibration curve may result in significant retention time shifts; therefore, all peaks, which have significant areas and elute closely to a target compound should be tentatively identified as a target compound and evaluated as such. Peaks over-range are handled using dilutions as detailed above (10.5.2).

11.1.1 Evaluate the internal standard (if used) and the surrogates to check for shifts in retention times and to evaluate the surrogate recovery. The recovery criteria for surrogates are given in the STL LQM.

Internal Standard Criteria

The internal standard must be within the retention time window defined by the associated CCV. The response of the internal standard(s) must be within a range +/–50% of the response of the internal standard in the associated CCV.

If sample matrix interferences preclude the use of internal calibration for a sample extract, two options should be considered:

1) dilute the extract or perform sample extract cleanup to minimize or eliminate the interference
2) use external standard calibration to quantify the target and surrogate compounds (if external standard calibration is used, all calibration requirements, including a capping standard, must be met-see Appendix C for the external standard sequence).

Surrogate Criteria

A minimum of two surrogates is spiked into each sample and QC item prior to preparation. Decachlorobiphenyl (DCB) and 2,3,4,6-tetrachloro-m-xylene (TCMX) are the recommended surrogates. DCB should be evaluated as the primary surrogate; TCMX is evaluated if there is matrix interference with DCB.

Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Evaluate the surrogates in the same manner as the target compounds using the guidance in the table in Section 11.1.3.

NOTE: If the recovery of the surrogate(s) is above the upper control limit and no target compounds are detected in the sample, results may be reported. Refer to STL SOP AN02 regarding this issue.

Dilutions and Surrogate Recovery

The concentration range for surrogates is one approximately 0.0025ug/mL to 0.080ug/mL. This should give us up to a six-fold dilution to report surrogate recoveries if the spiking level is 0.5ug/L and the lower limit of quantitation is 0.025ug/L. The lower recovery limit is 30%, therefore the lowest acceptable concentration is 0.5*0.3=0.15ug/L. The highest dilution to report un-qualified results ("J" flag) would be 0.15ug/L/0.025ug/L = 6 or a six fold dilution.

11.1.2 Evaluate each peak that corresponds to a target compound. Observe the general appearance of the chromatogram for possible dilutions, matrix interferences, and the overall shapes of the peaks.

If the concentration is below the lowest calibration standard or MDL (if the sample is being evaluated for "J" results), the reporting limit (RL) for that compound is calculated (Section 11.2). The RL is calculated for all target compounds that are not detected on the primary analytical column. Peaks over-range are handled using dilutions as detailed above (10.5.2).

NOTE: If a peak is over range on the primary column, evaluate the confirmation column. If no peak is detected or if the concentration is within the calibration range with the %RPD >40, the analysis at a dilution is not necessary.

11.1.3 If the result for a target is above the reporting limit (RL) on the primary column, evaluate the confirmation column. Use the retention time window calculated using the CCV as guidance for the identification of the target compounds. Note shifts in the retention times of the surrogate compounds or internal standard(s) to help gauge possible shifts in the RT of the target compounds. If, in the professional judgement of the analyst and supervisor, a peak within the retention time window can be reasonably excluded as a target, the result may be reported as a "non detect".

If the target compound is detected on the confirmation column, the concentration of the target compound is calculated and compared to the result from the primary column. The relative percent difference is calculated:

$$\%RPD = \left| \frac{(Cprim - Cconf)}{\frac{(Cprim + Cconf)}{2}} \right| \otimes 100$$

Where
Cprim = concentration of the target compound on the primary column
Cconf = concentration of the target compound on the confirmation column

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If the relative percent difference is less than or equal to 40%, the presence of the target compound is confirmed and the higher concentration is reported.

NOTE: The relative percent difference between any two numbers will be a maximum of 200%. A larger relative percent difference may be acceptable at concentrations near the reporting limit. If in doubt about whether to report a peak as a quantitative result, consult the section supervisor.

If the %RPD is greater than 40%, evaluate the chromatograms to determine if matrix interferences are present on one or both columns. Flag the result to note the disparity (P flag) between the results. Alternatively, perform additional extract cleanup (sulfur, florisil, etc.) or if cleanup is not feasible or there is a low probability that cleanup will help, dilute the extract to a level that removes the interference and report the RL from this dilution.

The default guidance in this table assumes the following:
1) the retention time and response of the internal standard(s) are within acceptance criteria with little or no shift in RT
2) surrogate recovery meets the acceptance criteria and peaks fall within the middle of it's retention time window with little or no shift in RT
3) the peak identified as the target falls in the middle of the retention time window for that compound

Default Guidance for Evaluation of Surrogates and Target Compounds in Samples, LCS, and MS

PEAK INFORMATION	COLUMN 1	COLUMN 2	%RPD	REPORT
No peak present	No peak		NA	<RL If compound is a surrogate, re-extract. If sample is LCS, re-extract.
		No peak	NA	
Peak present at RT	<E	<E	<=40%	Report highest
	<E	<E	>40%	Report result most appropriate for sample matrix. Use lowest result as default. Flag with "P"
Peak present at RT	>E	<E	<=40%	Dilute extract to get both results within the calibration curve.
	<E	>E		
	>E	<E	>40%	Report lowest result and flag with "P" No dilution required.
	<E	>E		

E = highest point in curve above which results are flagged as "E". The concentration range for target compounds is RL or MDL to E. Flag results <RL but >MDL as "J". Report result less than MDL as <RL.

MS/MSD Evaluation
If the concentration of a target analyte in the un-spiked (native) sample is more than four times the theoretical concentration of the matrix spike, the recovery is not reported and the data are flagged.

11.1.5 Identification "Tools"
Analysis by GC/MS (scan or SIM) may be used to confirm the presence of the target compounds (see STL SOP SM06: *Guidelines for SIM Analysis by GC/MS.)*

11.1.5.1 Relative Retention Time

The retention time of a surrogate compound or internal standard provides useful information about the stability of the GC system. If the surrogate RT has not changed, it is probable that the target analytes RTs have not changed. The relative retention time can help the analyst to evaluate a peak:

$$RRT = \frac{RT_{target}}{RT_{surrogate}}$$

The relative retention time will remain fairly constant under the same GC conditions. The expected retention time of the target can be estimated from the RRT and the RT of the reference (in this case, the surrogate):

$$RT_{target} = RRT \times RT_{surrogate}$$

The analyst must be alert for the presence of matrix interferences and evaluate the data on both columns before making an identification. Another useful tool that employs a similar idea to the RRT is to "overlay" the sample chromatogram with the calibration standard. If the *chromatograms are scaled the same, the overlay provides good visual cues to the identification of* the target compound.

11.1.5.2 Co-Injection

Another useful "tool" is to add a known amount of the target analyte to a portion of the extract. The analysis of this "fortified extract" may provide chromatographic information that supports or refutes the initial identification. The analyst is cautioned to use this approach with discretion and with consultation with the GC supervisor. As a general rule, spike a portion of the extract with an amount of target analyte that will result in about a 2-fold increase in response.

NOTE: Do not perform this procedure until you have exhausted all other avenues and have consulted with the GC supervisor or other manager with GC experience.

11.1.6 Qualitative Analysis of Multiple Peak Compounds

Identification of multi-peak pesticides (Toxaphene and Technical Chlordane) and PCBs as Aroclors is based on the recognition of their chromatographic patterns. Quantitation is performed using the area of characteristic peaks in the sample and standard using external or internal calibration procedures.

If compound identification or quantitation is precluded due to interference (e.g., broad, rounded peaks or ill-defined baselines are present) cleanup of the extract may be warranted. Suggested cleanup options are given in Section 9.

11.1.5.1 PCBs as Aroclors

PCBs are generally reported as Aroclors. The Aroclors have varying levels of PCB congeners with the last two numbers in the Aroclor designation indicating the weight percent of chlorine. For example, AR1221 is 21% chlorine by weight; AR1260 is 60% chlorine by weight. The 12- in the Aroclor designation represents the biphenyl molecule. The exception to this naming convention is AR1016, which is about 42% chlorine by weight. (Note that AR1016 and AR1242 have similar chromatograms - both Aroclors have almost the same weight of chlorine by weight and nearly the same PCB congeners.)

Aroclors are identified by matching the pattern of the sample with standards analyzed under the same analytical conditions. Interference may occur due to the presence of non-target analytes or due to "weathering" of the Aroclor in the environment. The presence of multiple Aroclors will also complicate identification and quantitation. Many matrix interferences may be reduced or eliminated by treating the sample extract with copper, sulfuric acid, and permanganate prior to analysis. STL SL SOP EX60 details this procedure.

NOTE: Do not use the acid or permanganate cleanup on the entire extract if pesticides are also to be reported as many of the pesticides are not stable in acid or strong oxidizer.

When a pattern matching an Aroclor is encountered, it may be quantitated using either the 3-5 characteristic peaks (recommended) or total area response. Total area quantitation should only be used as detailed below. Residues of either AR1016 or AR1260 are quantitated using the average RF/CF determined during initial calibration. The other Aroclors are quantitated against the RF/CF determined from their single-point analysis during initial calibration. Samples should be diluted when the amount of PCB in a sample extract exceeds the calibration range defined in initial calibration. Note that the AR1660 standard defines the working range for all the Aroclors. (i.e. if AR1660 was calibrated from 0.10ug/mL to 5.0ug/ml, and a sample extract was analyzed containing 10ug/ml of AR1232, that extract would require dilution to get the amount of AR1232 to be less than 5.0ug/ml.) If a sample contains any of the single point Aroclors (that is, Aroclors other than AR1016 and AR1260), then that associated standard must be run within 72 hours of the sample to determine retention time shifts.

In the 3-5 peak approach, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of PCB in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 3-5 resulting concentrations are averaged to provide the final result for the sample.

"Weathering" is the loss of part of the Aroclor pattern due to biological or chemical degradation of individual PCBs. When weathering is suspected, try to match the later eluting peaks first. Flag the results for a weathered Aroclor pattern as tentatively identified and make a note in the case narrative if provided.

The presence of multiple Aroclors can be a problem to identify since most Aroclors have at least a few PCBs in common. The easiest case would be to have early and late eluting Aroclors present. The most difficult cases will involve the presence of Aroclors with the same relative chlorine level. In cases where the identification of Aroclors cannot be clearly determined, quantify the Aroclors against the Aroclor that most closely matches the pattern of the sample using the total area of all peaks within the pattern range. The result should be flagged and noted in the case narrative if provided.

NOTE: When choosing individual peaks for quantitation, compare their responses in the sample and standard. If the peaks chosen do not correlate well (i.e. ratios to other peaks are close) between the sample and standard, review the chromatograms for other possible peaks for quantitation.

A Quick Check for Reasonableness-Quantitation of Multiple Component Pesticides and PCBs

If individual peaks from the multiple component compounds (Toxaphene, Technical Chlordane, and PCBs as Aroclors) are used to quantify samples, it may be difficult to determine whether the average of these peaks reasonably represents the concentration of these target compounds. Use the total area of the multiple component compound to determine if the quantitation is reasonable. If multiple Aroclors are present, use the Aroclor that most resembles that pattern.

1) Determine the retention time range for the target compound from the standard.
2) Determine the total area under the pattern for the peaks within the retention time range for the sample and last single point standard from the ICAL or CCV.
3) Calculate the calibration factor from the single point standard:

$$CF = \frac{Total\ Area}{Concentration(ug/mL)}$$

4) Calculate the concentration of the target compound in the sample using the single point CF:

$$ug / L = \frac{Total\ Area}{CF} \otimes \frac{F(mL) \otimes DF}{V(L)}$$

where
CF = defined above
Total Area (Sample) = area from the sample pattern
F = final volume of extract (mL)
DF = dilution factor
V = volume of sample extracted (L)
(For soils, change V to W, where W= weight of sample extracted in kg on dry weight basis)

5) Compare the concentration calculated from the individual peaks to the concentration calculated from the total area. If these concentrations agree within a factor of two, the results for the individual peaks can reasonably be reported. If not, consult the supervisor and technical manager to develop a strategy for quanting the samples. If you decide to use total area to report the samples, the initial calibration for the target compounds must also be re-evaluated using total area.

11.1.5.2 Toxaphene

Toxaphene is a mixture of chlorinated camphenes, which has a complex and characteristic pattern when analyzed by GC-ECD. A single Toxaphene standard is analyzed during the initial calibration for the purpose of pattern identification in samples. When a Toxaphene residue is detected in sample(s), sample analysis is stopped. A calibration curve with at minimum of 5 points bracketing the instrument calibration range for Toxaphene should be analyzed. Alternatively, single points may be prepared with Toxaphene concentrations within 2x the Toxaphene quantity detected in the samples. Generally, the calibration curve option is simpler. After analysis of the Toxaphene standard(s), the samples are re-analyzed using this standard(s) for quantitation. Note that when analysis of Toxaphene-containing samples occurs over an extended time, the calibration factor should be verified or regenerated every 12 hours.

If the sample and standard chromatograms agree well, Toxaphene is quantitated using 5 characteristic peaks (similar to the PCB approach, above). If the sample and standard pattern do not agree as well (i.e. individual peak ratios do not agree as well, but all the major Toxaphene components in the standard are present in the sample), a total area integration is more appropriate. To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the retention times of the first and last eluting Toxaphene components in the standard. Note that in order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample and that extraneous peaks or humps (contributed by non-Toxaphene components) are NOT included in the quantitation.

When Toxaphene is determined using the 5 peak approach, the analyst must take care to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms. It is highly unlikely that the peaks will match exactly, but the analyst should not employ peaks from the sample chromatogram whose relative sizes or areas appear to be disproportionately larger or smaller in the sample compared to the standard.

In the 5-peak approach, use each peak in the standard to calculate a calibration factor for that peak, using the total mass of Toxaphene in the standard. These calibration factors are then used to calculate the concentration of each corresponding peak in the sample chromatogram and the 5 resulting concentrations are averaged to provide the final result for the sample.

11.1.5.3 Chlordane

Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. The following components are significant: α and γ Chlordane, trans-Nonachlor, Heptachlor, and Heptachlor-epoxide. The α and γ Chlordane isomers are the most prevalent and their detection as single components is a good indicator that Technical Chlordane may be present.

When the GC pattern of the residue resembles that of the Technical Chlordane standard, quantitate Chlordane residues by comparing the area of 3 to 5 major peaks. Heptachlor and heptachlor epoxide should not be included in this quantitation but rather should be quantitated and reported separately.

When a Technical Chlordane residue is detected in sample(s), sample analysis is stopped. A calibration curve with at minimum of 5 points bracketing the instrument calibration range for technical chlordane should be analyzed. Alternatively, single points may be prepared with technical chlordane concentrations within 2x the Technical Chlordane quantity detected in the samples. Generally, the calibration curve option is simpler. After analysis of the technical chlordane standard(s), the samples are re-analyzed using these standard(s) for quantitation. Note that when analysis of technical chlordane-containing samples occurs over an extended time, the calibration factor should be verified or regenerated every 12 hours.

NOTE: These procedures are not necessary if the lab is reporting chlordane as the α and γ chlordane isomers, not as the technical product.

11.2 Calculations-see SOP AN67: *Evaluation of Calibration Curves* for the calculations of sample concentrations.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The **analytical batch** is discussed in STL SOP AN02: *Analytical Batching*, and these criteria are summarized in the SOP Summary included in Appendix C. Calculation of QC data is also given in AN02.

12.2 The **method detection limit (MDL)** must be determined annually in each matrix of concern in accordance with STL SOP CA90: *Procedure for Determination of Method Detection Limit (MDL).*

12.3 Each analyst must participate (individually or as part of a work group) in the analysis and evaluation of QC samples to demonstrate proficiency in this procedure. The IDOC samples are processed in the same manner as routine samples and evaluated according to STL SOP CA92.

13.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

No items are included in this revision.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

15.0 REFERENCES

1. *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; including Update III. U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.

2. *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office: Washington, DC, July 1, 1988.

Appendix A

TABLE 1		
Compound	RT COL 1	RT COL 2
Tetrachloro-m-xylene	5.26	6.65
Alpha-BHC	7.39	7.71
Gamma-BHC (Lindane)	8.63	8.65
Beta-BHC	8.80	8.39
Heptachlor	9.54	10.61
Delta-BHC	9.83	9.19
Aldrin	10.38	11.53
Heptachlor epoxide	11.96	12.51
Gamma-Chlordane	12.31	13.04
Alpha-Chlordane	12.72	13.41
Endosulfan I	12.86	13.42
4,4'-DDE	13.39	13.84
Dieldrin	13.63	14.05
Endrin	14.45	14.53
4,4'-DDD	14.75	14.83
Endosulfan I	14.97	14.78
4,4'-DDT	15.54	15.78
Endrin aldehyde	15.76	15.21
Endosulfan sulfate	15.98	15.71
Dibutyl chlorendate	16.73	17.80
Methoxychlor	17.60	17.04
Endrin ketone	17.79	16.82
Decachlorobiphenyl	21.36	22.36
Technical chlordane	MR	MR
Toxaphene	MR	MR
AR 1221	MR	MR
AR1232	MR	MR
AR1016	MR	MR
AR1242	MR	MR
AR1248	MR	MR
AR1254	MR	MR
AR1260	MR	MR
Isodrin	11.85	12.45
Chlorobenzilate	14.51	14.79
AR1268	MR	MR

MR = multi-peak/multi-response compounds COL1 = DB608 COL2 = DB-5

Appendix B: CHLORINATED PESTICIDES AND PCBs STANDARDS

Routine Targets

Target compound	ISMA-1 (ug/mL)	ISMA-2 (ug/mL)	ISMA-3 (ug/mL)	ISMA-4 (ug/mL)	ISMA-5 (ug/mL)
TCMX, DCB (surr)	0.0025	0.0050	0.010	0.020	0.040
g-BHC(Lindane), Heptachlor, Heptachlor epoxide, Endosulfan I	0.0050	0.010	0.020	0.030	0.050
Dieldrin, p,p'-DDT, Endosulfan II, Endrin aldehyde, Methoxychlor	0.010	0.020	0.040	0.060	0.10

Target compound	ISMB-1 (ug/mL)	ISMB-2 (ug/mL)	ISMB-3 (ug/mL)	ISMB-4 (ug/mL)	ISMB-5 (ug/mL)
TCMX,DCB (surr)	0.0025	0.0050	0.010	0.020	0.040
a-BHC, b-BHC, d-BHC, a-Chlordane, g-Chlordane,	0.0050	0.010	0.020	0.030	0.050
p,p'-DDE, Endrin p,p'-DDD, Endosulfan sulfate, Endrin ketone	0.010	0.020	0.040	0.060	0.10

DDT/Endrin Breakdown Evaluation Standard

Pesticide Evaluation Standard	CONC (ug/mL)
Endrin,	0.040
P,P'-DDT	0.040

Appendix IX Targets

Target compound	ISMB-1 (ug/mL)	ISMB-2 (ug/mL)	ISMB-3 (ug/mL)	ISMB-4 (ug/mL)	ISMB-5 (ug/mL)
TCMX,DCB (surr)	0.0025	0.0050	0.010	0.020	0.040
Isodrin	0.0050	0.010	0.020	0.030	0.050
Chlorobenzilate	0.050	0.10	0.20	0.50	1.0
Kepone	0.025	0.050	0.10	0.20	0.50

APPENDIX B

Technical Chlordane Five-point Curve

STOCK STANDARD	TCHLOR -1	TCHLOR -2	TCHLOR -3	TCHLOR -4	TCHLOR -5
Technical Chlordane	0.10	0.20	0.40	0.60	0.80
DCB, TCMX (surr)	0.0025	0.0050	0.010	0.020	0.040

Toxaphene Five-point Curve

STOCK STANDARD	TOX -1	TOX -2	TOX -3	TOX -4	TOX -5
Toxaphene	0.10	0.20	0.40	1.0	2.0
DCB, TCMX (surr)	0.0025	0.0050	0.010	0.020	0.040

PCBs as Aroclors

AR1660 Standards

Calibration Std	AR1016(ug/mL)	AR1260(ug/mL)	surrogates
AR1660-1	0.10	0.10	0.0025
AR1660-2	0.20	0.20	0.0050
AR1660-3	0.50	0.50	0.010
AR1660-4	1.0	1.0	0.020
AR1660-5	2.0	2.0	0.040

Single Point Aroclor Calibration Standards

Calibration Standard	Single Pont Concentration (ug/mL)	Surrogate Concentrations (ug/mL)
AR1221	1.0	0.020
AR1232	1.0	0.020
AR1242	1.0	0.020
AR1248	1.0	0.020
AR1254	1.0	0.020

If required, five point curves for AR1221, AR1232, AR1242, AR1248, and AR1254 are prepared at the same concentrations as the AR1660 curve.

Appendix C

METHOD 608 SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage*	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	None; 4C	1-L amber	7 days	40 days

*Storage temperature is 4C with control criteria of less than 6C with no frozen samples

EXTRACTION

Aqueous: Approximately 1L of sample (contents of container) using continuous or separatory funnel extraction at pH 5-9 with methylene chloride; exchange to hexane and concentrate to final volume of 10mL

ANALYSIS

Dual capillary columns with dual EC; 2-5uL injection into glass tee or y-splitter; external or internal standard calibration

SURROGATE(S):

Tetrachloro-m-xylene- 0.50ug/L
Decachlorobiphenyl-0.25ug/L

BATCH QC

Method blank
LCS/LCSD- full target list of single peak analytes @ 0.20ug/L
MS/MSD- full target list of single peak analytes @ 0.20ug/L

SEQUENCE-600-series (pesticides and PCBs)

Endrin/p,p'-DDT breakdown evaluation (daily-every 24 hours)
Initial Calibration- 3 point single peaks compounds 1 point all Aroclors 1 point toxaphene 1 point technical chlordane
Initial Calibration Verification (ICV)
Sample analyses
Continuing calibration verification (CCV)-daily-every 24 hours Single peak compounds AR1660
RL standard(optional; required by state or client QAP)
Sample analyses

Sequence continues until all samples have been analyzed or the CCV fails the acceptance criteria. If a multi-peak target compound is detected, the extract is reanalyzed with a 3-point curve.

SEQUENCE-600-series (pesticides only)

Endrin/p,p'-DDT breakdown evaluation (daily-every 24 hours)
Initial Calibration- 3 point single peaks compounds 1 point toxaphene 1 point technical chlordane
Initial Calibration Verification (ICV)
Sample analyses
Continuing calibration verification (CCV)-daily-every 24 hours Single peak compounds
RL standard(optional; required by state or client QAP)
Sample analyses

Sequence continues until all samples have been analyzed or the CCV fails the acceptance criteria. If a multi-peak target compound is detected, the extract is reanalyzed with a 3-point curve

SEQUENCE-600-series (PCBs only)

Initial Calibration- 3 point AR1660 1 point remaining Aroclors
Initial Calibration Verification (ICV)
Sample analyses
Continuing calibration verification (CCV)-daily-every 24 hours AR1660
RL standard(optional; required by state or client QAP)
Sample analyses

Sequence continues until all samples have been analyzed or the CCV fails the acceptance criteria. If an Aroclor other than AR1016 or AR1260 is detected, the extract is reanalyzed with a 3-point curve of the Aroclor detected.

Appendix C

METHOD 8081A AND 8082 SUMMARY

HOLD TIMES

MATRIX	Preservative/ Storage*	Routine Container	Sample Hold Time	Extract Hold Time
Aqueous	None; 4C	1-L amber	7 days	40 days
Soil/ Sediment	None; 4C	500-mL	14 days	40 days
Waste	None; 4C	Glass	14 days	40 days
TCLP	None; 4C	1-L amber	7 days (after leaching procedure)	40 days

*Storage temperature is 4C with a control criteria of less than 6C with no frozen samples

EXTRACTION

Aqueous: Approximately 1L of sample (contents of container) using continuous or separatory funnel extraction at pH 5-9 with methylene chloride; exchange to hexane and concentrate to final volume of 10mL
Soil/Solids: Approximately 30g of sample using sonication with 1:1 acetone/hexane or 1:1acetone/methylene chloride; Concentrate to final volume of 10mL in hexane
Wastes: Approximately 1g of sample diluted to final volume of 10mL with hexane

ANALYSIS

Dual capillary columns with dual EC; 2-5uL injection into glass tee or y-splitter; external or internal standard calibration

SURROGATE:	Aqueous(ug/L)	Soils(ug/kg)
Tetrachloro-m-xylene	0.50	15
Decachlorobiphenyl	0.50	15
Dibutyl chlorendate (optional)	0.50	15

BATCH QC

Method blank
LCS- LQM subset
MS/MSD- LQM subset

Parameter	Aqueous(ug/L)	Soils(ug/kg)
Lindane	0.20	6.0
Aldrin	0.20	6.0
Heptachlor	0.20	6.0
Dieldrin	0.50	15
Endrin	0.50	15
p,p'-DDT	0.50	15

Appendix C

The sequence continues until all samples have been analyzed or until the calibration verification fails the acceptance criteria. All sample extract analyses must be bracketed by acceptable verification standards if external standard calibration is used; if internal standard calibration is used, capping of the sequence by a CCV standard is not required unless specified in an agency or client QAPP. The default procedure is not to count the QC items in the 20 sample extracts that may be analyzed in the clock; i.e.; the number of sample and QC extracts may exceed 20 but the total number of sample extracts may not exceed 20 and all extracts (samples and QC) must be analyzed within the 12-hour clock.

SEQUENCE-8081A and 8082 (pesticides and PCBs)

STANDARD/SAMPLES
Endrin/p,p'-DDT breakdown (every 12 hours)
Initial Calibration- 5 point single peaks 5 point Ar1660(note1) 1 point Toxaphene 1 point technical Chlordane 1 point remaining Aroclors
Up to twenty sample extracts
Endrin/p,p'-DDT breakdown (every 12 hours)
Continuing calibration check midpoint single peaks and midpoint AR1660(note1)
RL Standard(optional)-lowest point on the calibration curve if required by state or client QAP
Up to twenty sample extracts
Endrin/p,p'-DDT breakdown (every 12 hours)
Continuing calibration check-midpoint single peaks and midpoint AR1660(note1)

Note 1-A mixture of AR1016 and AR1260 will be used to calibrate and verify the response for PCBs.

SEQUENCE-8081A (pesticides only)

STANDARD/SAMPLES
Endrin/p,p'-DDT breakdown (every 12 hours)
Initial Calibration- 5 point single peaks 1 point Toxaphene 1 point technical Chlordane
Up to twenty sample extracts
Endrin/p,p'-DDT breakdown (every 12 hours)
Continuing calibration check midpoint single peaks
RL Standard(optional)-lowest point on the calibration curve if required by state or client QAP
Up to twenty sample extracts
Endrin/p,p'-DDT breakdown (every 12 hours)
Continuing calibration check-midpoint single peaks

SEQUENCE-8082 (PCBs only)

STANDARD/SAMPLES
Initial Calibration- 5 point Ar1660(note1) 1 point remaining Aroclors
Up to twenty sample extracts
Continuing calibration check midpoint AR1660(note1)
RL Standard(optional)-lowest point on the calibration curve if required by state or client QAP
Up to twenty sample extracts
Continuing calibration check-midpoint Ar1660(note1)

Note 1-A mixture of AR1016 and AR1260 will be used to calibrate and verify the response for PCBs.

Appendix C

QC CHECK	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
p,p'-DDT and Endrin breakdown check -required for 8000-series, recommended for 600-series	Initially and every 12 hours	% breakdown of both compounds less than 15%	-re-analyze check solution -perform injector port and/or column maintenance and re-analyze
Initial Calibration- 600-series:3 point minimum with lowest point at RL 8000-series:5 point minimum with lowest point at RL	Initially prior to sample analysis, when major instrument maintenance performed, or when CCV fails	**600-series:** 1) RSD of each target <= 10%; OR 2) plot regression curve CC>=0.99 for each target **8000-series:** 1) RSD of each target <= 20%; OR 2) plot regression curve CC>=0.99 for each target (see previous page for exceptions)	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Continuing calibration verification(CCV) (NOTE: The default procedure is to cap external standard calibrations with CCV and ***not*** to cap internal standard calibrations with CCV. Check the pre-project plan or client QAPP to determine if capping is required for internal standard calibrations.)	**External Standard Calibration**: After every ten to twenty sample analyses and at the end of the sequence 8000-series: the capping standard must be injected within 12-hours of the last standard in the ICAL or within 12 hours of the previous CCV **Internal Standard Calibration**: Prior to every ten to twenty sample analyses-capping is not required No more than 12 hours can elapse between CCV and the last sample in the sequence.	-Percent difference or drift <= 15% (see SOP for use of "grand mean") -Response of the internal standard must be within a range of +/−50% of the mid-level standard (CCV) in the ICAL	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards

Appendix C

QC CHECK	FREQUENCY	ACCEPTANCE CRITERIA	CORRECTIVE ACTION
Method blank	Per batch	All targets reported less than RL in LQM	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL SOP AN02
Lab control sample (LCS)- Subset of targets in STL SL LQM	Per batch (If MS/MSD cannot be performed, the LCS must be performed in duplicate)	Recoveries within LQM limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL SOP AN02
Matrix spike(MS) and matrix spike duplicate (MSD)	Per batch	Recoveries within LQM limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL SOP AN02
Internal Standard Response	All samples, method blanks, and QC	-response within a factor of +/–50% of the previous CCV -retention time within window defined by previous CCV	-Evaluate chromatogram and integrations. -Reanalyze or dilute and reanalyze -Flag data
Surrogates	All samples, method blanks, and QC	Recoveries within LQM limits See section 11.1.1. for specifics	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in STL SOP AN02
Dilutions	When extract concentration exceeds calibration range	Report dilution where highest concentration target is in upper half of calibration range (see Section 10.5.2 for further guidance)	-Dilute sample to bring highest concentration into upper half of calibration range. Report all other targets from this dilution. -If lower RL required, prepare dilution 1/10 of dilution that puts highest concentration target into upper half of calibration range.

Appendix C

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Reporting limit(RL) standard-standard at the reporting limit used to verify sensitivity of the instrument	Daily(optional-see specific state or client requirements for frequency)	Detected with reasonable sensitivity	-Reanalyze RL standard -Remake and reanalyze RL standard -Perform instrument or column maintenance, recalibrate, and reanalyze associated samples
Retention time window determination	See guidance in STL SOP AN66	See guidance in STL SOP AN66	Use guidance in STL SOP AN66: *Determination of Retention Time Windows in Gas Chromatographic Analyses*
Initial demonstration of Capability (the analyst has to perform the IDOC for either of the analogous 600 or 8000 series methods- not both)	Per work group or analyst	Within the 600- or 8000-series method limits (see STL SOP CA92)	-Reanalyze QC sample for the targets that failed to meet the criteria (see STL SOP CA92)
Method detection limit(MDL)	See STL SOP CA90	Evaluate data using criteria STL SOP CA90	-Evaluate data. Check calculations. -Reanalyze MDL samples.

SEVERN TRENT STL

CHLORINATED HERBICIDES
(Methods: 515.1, 615, and 8151A)

Approved by:

Andrea Teal — 11/06/02

Date

Title: Quality Assurance Manager

STL ✓ Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

1.1 This SOP describes the procedures used to determine the concentration of chlorinated herbicides in various matrices. Appendix A contains an example of the retention time order for the herbicides, Appendix B provides examples of the calibration standards routinely analyzed, and Appendix C contains a summary of the method QC requirements for Methods 515.1, 615, and 8151A.

Method	Routine Matrices
515.1	Drinking water
615	Water and Wastewater
8151	Water, groundwater, soils, solids, wastes, leachates

1.2 The routine target compounds, reporting limits (RL), the method detection limits (MDL), and the accuracy and precision criteria are listed in the current revision of the laboratory quality manual (LQM).

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Environmental samples are prepared using the procedures outlined in SOP EX45: *Extraction of Chlorinated Herbicides.* The extracted methyl derivatives are analyzed by a GC equipped with dual capillary columns (different phases) connected to dual electron capture (EC) detectors, allowing simultaneous detection and confirmation of the target compounds. Quantitation may be performed using the external or internal standards calibration technique.

2.2 GC/MS confirmation can also be employed if analyte concentration is sufficiently high or if the sample extract is concentrated to an appropriate final volume. The esterified extract must be used for the GC/MS confirmation – do not use the 8270 extract.

2.3 Method Clarifications/Default Procedures

Elimination of Calibration Points: When more calibration standards are analyzed than required, individual compounds may be eliminated from the lowest or highest concentration level(s) only. If points or levels are eliminated, analyte concentration in samples must fall within the range defined by the resulting curve. In no case should individual points in the middle of a calibration be eliminated without eliminating the entire level.

Bracketing Sample Extracts: The default procedure for continuing calibration verification for the 8000-series methods is to bracket samples by CCV standards (before and after) if external standard calibration is used and ***not*** to cap the sequence (run CCV after the samples) if internal standard calibration is used ***unless*** noted in the client QAPP or in an STL pre-project plan. The internal standard provides verification information on the sensitivity and retention time stability of the instrument and verification of acceptable injections of the sample extracts. See Appendix C for summaries of the analytical sequences.

Grand Mean: The "grand mean" is used to evaluate calibration data according to the provisions of SW-846 Method 8000B and Sections 10.3 and 10.4 of this SOP.

Dilutions: Unless otherwise specified by a client or QA plan, results from a single dilution are reportable as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client.

For clients who demand lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 the dilution factor with the highest target in the upper half of the calibration curve. For example, a sample analyzed at a DF of 50 resulting in a hit in the upper half of the calibration curve would be reanalyzed at a DF of 5 to provide lower detection limits to the client. Project managers and lab staff must work together to balance client satisfaction with productivity.

2.4 This method is based on the guidance in SW-846 Methods 8000B, 8151A, 40 CFR 136 Method 615, and EPA method 515.1.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially hazardous situations.

3.2 The analyst should wear an apron or lab coat, gloves, and eye protection when handling extracts. Dilutions should be performed under a hood or in a well-ventilated area.

3.3 The analyst must be familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in the analysis of pesticides and PCBs. Many of these compounds are suspected carcinogens.Diethyl ether is a flammable solvent and it must be used in a well-ventilated hood or extraction area. The solvent vapors will tend to accumulate along the floor. High concentrations of diethyl ether can cause drowsiness, dizziness, and headache.

4.0 INTERFERENCES

4.1 Glassware should be scrupulously cleaned and solvent-rinsed in accordance with SOP AN60: *Glassware Cleaning Procedures* to minimize artifacts and/or elevated baselines in gas chromatograms. Any vessel that comes in contact with the extract is a potential source for contamination. Method blanks that are extracted and analyzed with each batch of samples will provide clues to the source of contamination from the glassware and reagents.

4.2 Matrix interferences may be caused by contaminants that are co-extracted from the sample. The sample may require dilution prior to analysis to reduce or eliminate interferences. The extraction procedure SOP EX45 has several steps that are designed to eliminate or minimize interferences due to matrix.is diluted as needed for data analysis. If a cleanup is used, the method blank must also be subjected to the cleanup.

4.3 Injection port maintenance is very important for the consistent detection of the reactive herbicides such as Dinoseb.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

See Appendix C for a summary of the sample collection, storage, and preservation requirements.

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph (GC), temperature programmable, equipped with single or dual electron capture (EC) detectors and a compatible autosampler

6.2 Data system compatible with the GC, with appropriate software or integration capabilities

6.3 The following column pairs are recommended. Other columns/phases may be used if the calibration and QC criteria are met and adequate separation of the target compounds is achieved.

Restek CLPesticides1 30 M x 0.32 mm ID x 0.5 um film
Restek CLPesticides2 30 M x 0.32 mm ID x 0.25 um film

6.4 Microsyringes: appropriate volumes

6.5 Volumetric flasks: Class A, appropriate volumes

6.6 Autosampler vials, septa, and caps: compatible with the autosampler

7.0 REAGENTS

Hexane - pesticide grade or equivalent, for preparation of standards

8.0 STANDARDS

8.1 The preparation of the calibration standards must be tracked in accordance with SOP AN41: *Standard Material Traceability*. General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation.*

8.2 The lab should purchase certified solutions from STL approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available. See SOP AN43 for guidance for standard preparation.

8.3 Herbicide standards are purchased as methyl esters; therefore, the concentration of the standard must be corrected to the free acid concentration. This will eliminate the need to correct the final concentration of the sample. The correction factors are given in Appendix D.

8.4 Calibration Standard Recipes

The recipes used for standard preparation must be clearly documented as a controlled posting or as a narrative in the traceability log. The lowest level calibration standard should be at or below the equivalent of the reporting limit as defined in the LQM or client QAPP. The remaining standards will define the working range of the analytical system. Appendix B contains example recipes of the calibration levels for the routinely determined herbicides.

9.0 SAMPLE PREPARATION

The sample preparation and cleanup procedures are described in SOP EX45

10.0 ANALYTICAL PROCEDURE

10.1 Gas Chromatograph Operating Conditions

The instrument conditions listed in this section are for guidance. The actual conditions used by the lab must be documented in the instrument maintenance log, data system, or run log. The goal is to have maximum separation between the target compounds in the shortest run time while maintaining sufficient sensitivity to detect the target compounds at the reporting limit and MDL (if required).

10.1.1 Two configurations are routinely used for the analysis of herbicides. A single column may be connected to the injection port or two columns may be connected to the injection port using a press-tight glass y-splitter and a guard column, a two-hole ferrule, or a glass tee to provide simultaneous detection and confirmation of the target analytes.

10.1.2 Example GC Parameters

Columns:
Restek CLPesticides1 30 M x 0.32 mm ID x 0.5 um film
Restek CLPesticides2 30 M x 0.32 mm ID x 0.25 um film
Injector: 220°C
Detector: 305 °C
Carrier Gas Flow: Helium at ~2mL/min (per column) (pressure at 20psi, constant)
Make-up Gas Flow: Nitrogen at ~60mL/min (per detector)

Temperature program:

Initial Temp:	40 C
Initial Hold:	0.50 min
Program Rate 1	12 C/min
HoldTemp 1:	200 C (hold for 4 minutes)
Program Rate 2	30 C/min
FinalTemp :	305 C (hold for 2 minutes)
TOTAL TIME	22.50 minutes

NOTE: These conditions and parameters are given for guidance. The columns/phases, GC conditions, and instrument parameters may be modified to optimize the analytical system.

10.2 Initial Calibration

Internal or external standard calibration techniques may be employed for the determination of the concentration of herbicides. The lab also has the option of using internal standard calibration. Pentachloronitrobenzene (PCNB) may be a suitable compound to use as an internal standard

10.2.1 Prepare and analyze the calibration standards. Injector port and column maintenance should be performed on the instrument prior to the analysis of the initial calibration standards. Guidance for establishing the analytical sequence is given in the SOP Summary.

Note that the following offers two (2) options for calibration and quantitation – average CF or regression curve. Only one needs be chosen per analyte.

10.2.2 Evaluate the standard chromatograms. Some questions to ask at this point are:

>Is there contamination in the hexane blank? If so, has maintenance been performed on the instrument lately? Has the septum been changed? Is the column properly seated in the injector and detector ports?
>Did all of the standards inject properly? Are there peaks for each of the standards analyzed? Do the patterns look normal?
>Are the peaks symmetrical? Is there tailing or fronting?
>Are the areas of the peaks normal for the sensitivity setting being used?

Inspect each chromatogram to ensure that the peaks are properly identified and that the correct areas have been associated with the corresponding standard peak RT in the data system tabulation.

10.2.3 Evaluate the calibration curve in accordance with SOP AN67: *Evaluation of Calibration Curves.*

10.3 Initial Calibration Criteria:

515.1: If the relative standard deviation is less than 20% for the target compounds in the initial calibration, the calibration is considered linear through the origin and the average calibration factor may be used for quantitation.

615: If the relative standard deviation is less than 10% for the target compounds in the initial calibration, the calibration is considered linear through the origin and the average calibration factor may be used for quantitation.

8151-series: If the relative standard deviation is less than 20% for the target compounds in the initial calibration, the calibration is considered linear through the origin and the average calibration factor may be used for quantitation.

The preferred method of quantitation is the average response or calibration factor. If one or more compounds do not meet the %RSD criterion, the next option is to evaluate a regression curve (Section 10.2.5). The "grand mean exception" described below should be applied to 8151A initial calibrations only in extraordinary circumstances because of the difficulty of maintaining and providing documentation on an on-going basis.

8000-series ICAL *grand mean exception:*
If one or more compounds exceed the %RSD criteria, the average calibration factors can be used for quantitation if the average %RSD of ALL of the compounds (the grand mean) in the ICAL is less than or equal to 20% and no single compound has a %RSD greater than 60%.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required since the lab has demonstrated that the lowest standard in the calibration curve (the equivalent of the RL) can be detected.

Regression Curve Option: A calibration curve is established for each analyte by plotting the concentration along the x-axis and the corresponding response along the y-axis. If r^2 is greater than 0.99, the curve can be used to quantify samples. For 8000-series methods, a minimum of five points is required for a linear regression, six points for a second order curve, and seven or more for higher order fits. It is recommended to use only linear and quadratic (second order) curves for quantitation. See SOP AN67 for guidance on evaluation of calibration curves.

NOTE: Linear regression curves must be used for South Carolina DHEC compliance samples. See pre-project plans and client QAPPs for other exceptions to using non-linear curve fitting.

10.4 Calibration Verification

Calibration is verified at the frequency given in the SOP Summary. If external standard calibration is used, the following criteria apply to calibration standards analyzed before and after samples. In situations where compounds fail criteria high and no positive hits for the compound(s) failing high are detected, these samples may be reported.

If internal standard calibration is used, the samples do not have to be bracketed (capped) by the analysis of a CCV standard unless specified by a regulatory agency or client QAPP.

10.4.1 Analyze a mid-level standard. The concentration of the verification standard should be varied periodically to evaluate the calibration curve in the lower and upper halves. Tabulate the area of the target analytes and calculate the response factors if using the average RF/CF option. If using the calibration curve option, calculation of the RF is unnecessary.

Calculate the percent drift or percent difference between the initial and continuing calibration in accordance with SOP AN67.

10.4.2 Continuing Calibration Verification Criteria

Response Criteria
If the CCV criterion is not met, another CCV should be analyzed. Repeated failure may be a sign of instrument or standard degradation. If the calibration verification criteria cannot be met, a new initial calibration must be prepared, analyzed, and evaluated.

515.1: If the percent drift or percent difference is less than or equal to 20%, the initial calibration is verified and the average response factor or regression curve can be used for quantitation.

615: If the percent drift or percent difference is less than or equal to 15%, the calibration curve is verified and the average response factor or regression curve can be used for quantitation.

8151: If the percent drift or percent difference is less than or equal to 15%, the calibration curve is verified and the average response factor or regression curve can be used for quantitation.

8000-series CCAL grand mean exception:
If one or more compounds exceed the %drift or %difference criteria, the average calibration factor or regression curve from the initial calibration can be used for quantitation if the average %drift or average % difference of ALL of the compounds (the grand mean) in the CCV is less than or equal to 15% and no single compound is greater than 45%D.

NOTE: If a target compound that passes by the "grand mean exception" is detected (>RL), the PM is notified via an anomaly report or case narrative. If the targets are <RL, no notification is required.

All samples analyzed using external standard calibration must be bracketed by acceptable CCV. If the CCV standard analyzed after the samples fails to meet the acceptance criteria and the response of the mid point standard is *above* the criteria (that is the response of the analytical system has increased), samples which have no target compounds detected above the RL may be reported as <RL, since the compounds would have been detected if present. (SW-846 Method 8000B).

Retention Time Criteria
The retention time for the CCV must fall within the daily retention time window as defined in SOP AN66: *Determination of Retention Time Windows for Gas Chromatographic Analyses.*

Internal Standard Response Criteria
If internal standard calibration is used, the response of the internal standard(s) must be within –50% to +150% of the response in the CCV-level standard in the initial calibration sequence. If the response is outside of this range, the analysis of the CCV must be repeated and any samples associated with the CCV must also be re-analyzed. Repeated failure of the ISTD response will require re-calibration.

RL Standard
An optional standard at the reporting limit (RL) may be analyzed in the analytical sequence to verify sensitivity of the target compounds. All target compounds in the RL standard should be recovered at 50-150% of its true concentration and all peaks should be adequately resolved. If the RL standard recovers within the specified limits, samples with no target compounds detected may be reported as such (i.e., less than the RL) regardless of whether the associated CCV passed the acceptance criteria.

10.5 Sample Analysis Sequence
The analytical sequences for the methods are given in the SOP Summary in Appendix C. The default is to exclude QC items (method blanks, LCS, and MS/MSD) in determining the maximum number of extracts in the clock. For 8151A, more than 20 extracts (samples and QC) may be analyzed in a sequence, as long as the 12 hour time frame has not elapsed, but the number of samples (non-QC extracts) may not exceed 20. Note that some client and agency QAPPs may require that the QC items be counted as part of the twenty samples.

10.5.1 The sample extract is injected using the same injection volume used for the calibration standards. Extracts that are known to be relatively clean should be analyzed first. Extracts suspected of containing high concentrations should be analyzed last. Instrument blanks may be analyzed after suspected high concentration samples to allow the detector response to stabilize.

10.5.2 If the concentration of target compounds exceeds the working range (defined by the highest standard in the initial calibration), the extract must be diluted in hexane and reanalyzed. A dilution should bring the area of the largest peak of interest into the upper half of the calibration curve. If the internal standard calibration is used, the concentration of the internal standard in the diluted extract must be the same as in the calibration standards.

NOTE: Unless otherwise specified by a client or QA plan, results from a single dilution are reportable as long as the largest target analyte (when multiple analytes are present) is in the upper half of the calibration range. When reporting results from dilutions, appropriate data flags should be used or qualification in a case narrative provided to the client.

For clients who demand lower detection limits, a general guide would be to report the dilution detailed above and one additional run at a dilution factor 1/10 the dilution factor with the highest target in the upper half of the calibration curve. For example, a sample analyzed at a DF of 50 resulting in a hit in the upper half of the calibration curve would be reanalyzed at a DF of 5 to provide lower detection limits to the client. Project managers and lab staff must work together to balance client satisfaction with productivity.

10.5.3 Occasionally, situations may arise where part of the chromatogram is obscured by large non-target peaks or matrix interferences (short, wide, peaks that are not well resolved). In these situations, it is permitted to report a lower RL for the target compounds that are not affected by the non-target or matrix interference and perform a dilution only for the target compounds that are affected. This anomalous situation must be discussed with the project manager and section supervisor prior to reporting the results and noted in the case narrative or anomaly report. Again, project managers and lab staff must work together to balance client satisfaction with productivity.

10.6 Determination of Retention Time Windows

The procedure for the determination of retention time windows is given in SOP AN66: *Determination of Retention Time Windows and Evaluation of Retention Time Data Chromatographic Analyses*. If internal standard calibration is used, the determination of absolute retention time windows is not required since relative retention times are used to identify the target compounds.

11.0 DATA ANALYSIS/CALCULATIONS

Methyl ester herbicide standards must be corrected to the free acid concentration. This is done by comparing the molecular weight of the methyl ester that of the acid ton determine a correction factor. Table 2 gives the molecular weights of the acids and esters. It also lists the correction factors and illustrates how to perform the acid-ester correction.

The evaluation of chromatograms for target compounds must take into account the calibration of the analytical system (initial and continuing calibration response and retention times); the recovery and retention time shift of the surrogate compounds, whether the peak response falls within the working range of the calibration; and the integration of the peaks. The analyst must also take into account the results from the method blank and lab control sample before reporting quantitative data. SOP AN66: *Determination of Retention Time Windows and Evaluation of Retention Time Data for Chromatographic Analyses* provides additional guidance for the evaluation of chromatographic data. This guidance is summarized in the following sections.

11.1 Compounds of Concern

Dalapon - this compound eluetes very early in the run and may be subject to interference from co-eluting compounds and from artifacts from the extraction process.

MCPA and MCPP - these compounds have very low response in comparison to the other herbicides.

Dinoseb - this compound can be lost in the extraction process (hydrolysis step) but also may be lost if the injection port is not frequently and properly maintained.

11.2 Manual integrations must be documented in accordance with SOP AN65: *Manual Integrations*. Data systems should be adjusted to minimize operator intervention. All chromatographic peaks must be evaluated for overall peak shape and "reasonableness" of integration. Under no circumstances should manual integrations be used to change reasonable data system integrations in order to meet calibration or QC criteria.

11.3 The judgement and experience of the analyst and his/her colleagues are important factors in the evaluation of chromatographic data. The analyst should ask:

- Is there previous data or current information about the sample that would aid in evaluating the data?
- Do the peaks look normal?
- Are peaks properly integrated?
- Are co-eluting peaks or matrix interferences present?
- Is the internal standard present at the correct retention time and response (-50% to150% of the response in the associated CCV)? Are the surrogates present at the expected RT or have they shifted?

Qualitative analysis

Identification of the surrogates and target compounds is based on retention time. The retention time (RT) windows calculated around the CCV retention times are used for the identification of the target compounds. The analyst should also note shifts in the retention times of the surrogate compounds or internal standard(s) to help gauge possible shifts in the RT of the target compounds. If, in the professional judgement of the analyst and supervisor, a peak within the retention time window can be reasonably excluded as a target, the result may be reported as a "non detect". This may only be done when the RT of the internal standard and surrogates are at their respective retention times and there is little or no evidence of matrix interferences. If there is doubt as to whether the peak can be excluded or not, the default procedure will be to report the peak as the target compound unless another technique (for example, GC/MS) is used to determine that the target compound is not present.

NOTE: It is important to note that the retention time window applies only to peaks that are within the calibration range of the curve. Peak areas that exceed the established linear range of the calibration curve may result in significant retention time shifts; therefore, all peaks, which have significant areas and elute closely to a target compound should be tentatively identified as a target compound and evaluated as such. Peaks over-range are handled using dilutions as detailed above (10.5.2).

Evaluate the internal standard (if used) and the surrogates to check for shifts in retention times and to evaluate the surrogate recovery. The recovery criteria for surrogates are given in the STL LQM.

Internal Standard Criteria

The internal standard must be within the retention time window defined by the associated CCV. The response of the internal standard(s) must be within a range +/–50% of the response of the internal standard in the associated CCV.

If sample matrix interferences preclude the use of internal calibration for a sample extract, two options should be considered:
1) dilute the extract to minimize or eliminate the interference
2) use external standard calibration to quantify the target and surrogate compounds (if external standard calibration is used, all calibration requirements, including a capping standard, must be met - see Appendix C for the external standard sequence).

Surrogate Criteria

DCAA is used as the surrogate for herbicide analysis. Given the complicated nature of GC-ECD chromatograms, assessing surrogate recovery is frequently complicated by co-eluting positive and negative interferences. Evaluate the surrogates in the same manner as the target compounds using the guidance in the table in Section 11.1.3.

NOTE: If the recovery of the surrogate(s) is above the upper control limit and no target compounds are detected in the sample, results may be reported. Refer to SOP AN02 regarding this issue.

Evaluate each peak that corresponds to a target compound. Observe the general appearance of the chromatogram for possible dilutions, matrix interferences, and the overall shapes of the peaks.

If the concentration is below the lowest calibration standard or MDL (if the sample is being evaluated for "J" results), the reporting limit (RL) for that compound is calculated (Section 11.2). The RL is calculated for all target compounds that are not detected on the primary analytical column. Peaks over-range are handled using dilutions as detailed above (10.5.2).

NOTE: If a peak is over range on the primary column, evaluate the confirmation column. If no peak is detected or if the concentration is within the calibration range with the %RPD >40, the analysis at a dilution is not necessary.

If the result for a target is above the reporting limit (RL) on the primary column, evaluate the confirmation column. Use the retention time window calculated using the CCV as guidance for the identification of the target compounds. Note shifts in the retention times of the surrogate compounds or internal standard(s) to help gauge possible shifts in the RT of the target compounds. If, in the professional judgement of the analyst and supervisor, a peak within the retention time window can be reasonably excluded as a target, the result may be reported as a "non detect".

If the target compound is detected on the confirmation column, the concentration of the target compound is calculated and compared to the result from the primary column. The relative percent difference is calculated:

$$\%RPD = \left| \frac{(Cprim - Cconf)}{\frac{(Cprim + Cconf)}{2}} \right| \otimes 100$$

Where
Cprim = concentration of the target compound on the primary column
Cconf = concentration of the target compound on the confirmation column

If the relative percent difference is less than or equal to 40%, the presence of the target compound is confirmed and the higher concentration is reported.

NOTE: The relative percent difference between any two numbers will be a maximum of 200%. A larger relative percent difference may be acceptable at concentrations near the reporting limit. If in doubt about whether to report a peak as a quantitative result, consult the section supervisor.

If the %RPD is greater than 40%, evaluate the chromatograms to determine if matrix interferences are present on one or both columns. Flag the result to note the disparity (P flag) between the results. Alternatively, dilute the extract to a level that removes the interference and report the RL from this dilution.

The default guidance in this table assumes the following:
1) the retention time and response of the internal standard(s) are within acceptance criteria with little or no shift in RT
2) surrogate recovery meets the acceptance criteria and peaks fall within the middle of it's retention time window with little or no shift in RT
3) the peak identified as the target falls in the middle of the retention time window for that compound

Default Guidance for Evaluation of Surrogates and Target Compounds in Samples, LCS, and MS

PEAK INFORMATION	COLUMN 1	COLUMN 2	%RPD	REPORT
No peak present	No peak		NA	<RL
		No peak	NA	If compound is a surrogate, re-extract. If sample is LCS, re-extract.
Peak present at RT	<E	<E	<=40%	Report highest
	<E	<E	>40%	Report result most appropriate for sample matrix. Use lowest result as default. Flag with "P"
Peak present at RT	>E	<E	<=40%	Dilute extract to get both results within the calibration curve.
	<E	>E		
	>E	<E	>40%	Report lowest result and flag with "P" No dilution required.
	<E	>E		

E = highest point in curve above which results are flagged as "E". The concentration range for target compounds is RL or MDL to E. Flag results <RL but >MDL as "J". Report result less than MDL as <RL.

MS/MSD Evaluation
If the concentration of a target analyte in the un-spiked (native) sample is more than four times the theoretical concentration of the matrix spike, the recovery is not reported and the data are flagged.

11.4 Identification "Tools"
Analysis by GC/MS (scan or SIM) may be used to confirm the presence of the target compounds (see SOP SM06: *Guidelines for SIM Analysis by GC/MS.)*

11.4.1 Relative Retention Time

The retention time of a surrogate compound or internal standard provides useful information about the stability of the GC system. If the surrogate RT has not changed, it is probable that the target analytes RTs have not changed. The relative retention time can help the analyst to evaluate a peak:

$$RRT = \frac{RT_{target}}{RT_{surrogate}}$$

The relative retention time will remain fairly constant under the same GC conditions. The expected retention time of the target can be estimated from the RRT and the RT of the reference (in this case, the surrogate):

$$RT_{target} = RRT \times RT_{surrogate}$$

The analyst must be alert for the presence of matrix interferences and evaluate the data on both columns before making an identification. Another useful tool that employs a similar idea to the RRT is to "overlay" the sample chromatogram with the calibration standard. If the chromatograms are scaled the same, the overlay provides good visual cues to the identification of the target compound.

11.4.2 Co-Injection

Another useful "tool" is to add a known amount of the target analyte to a portion of the extract. The analysis of this "fortified extract" may provide chromatographic information that supports or refutes the initial identification. The analyst is cautioned to use this approach with discretion and with consultation with the GC supervisor. As a general rule, spike a portion of the extract with an amount of target analyte that will result in about a 2-fold increase in response.

NOTE: Do not perform this procedure until you have exhausted all other avenues and have consulted with the GC supervisor or other manager with GC experience.

12.0 QUALITY ASSURANCE /QUALITY CONTROL

12.1 The **analytical batch** is discussed in SOP AN02: *Analytical Batching*, and these criteria are summarized in the SOP Summary included in Appendix C. Calculation of QC data is also given in SOP AN02.

12.2 The **method detection limit (MDL)** must be determined annually in each matrix of concern in accordance with SOP CA90: *Procedure for Determination of Method Detection Limit (MDL).*

12.3 Each analyst must participate (individually or as part of a work group) in the analysis and evaluation of QC samples to demonstrate proficiency in this procedure. The IDOC samples are processed in the same manner as routine samples and evaluated according to SOP CA92: *Evaluation of IDOCs.*

13.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

Refer to the instrument manufacturer's manual and SOP AN53: *Maintenance Procedures for Laboratory Instruments* for guidance on preventive maintenance and troubleshooting.

14.0 POLLUTION PREVENTION AND WASTE MANAGEMENT

Excess samples, extracts, reagent, and standards must be disposed of in accordance with SOP CA70: *Waste Management.*

15.0 REFERENCES

1. *Test Methods for Evaluating Solid Waste, Third Edition with Revisions and Updates, SW-846*; including Update III. U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC, November, 1986.

2. *Code of Federal Regulations, Title 40, Part 136*; U.S. Government Printing Office: Washington, DC, July 1, 1988.

APPENDIX A – Target Compounds and Retention Times

Compound	RT COL 1	RT COL 2
Dalapon	2.57	2.91
DCAA (surrogate)	10.22	10.88
Dicamba	10.30	11.06
MCPP	10.62	11.16
MCPA	10.90	11.59
Dichlorprop	11.30	11.91
2,4-D	11.62	12.40
2,4,5-TP (Silvex)	11.65	13.20
Pentachlorophenol	12.41	12.87
2,4,5-T	13.03	13.84
2,4-DB	13.67	14.54
Dinoseb	13.81	14.36
Picloram	14.76	17.46

COL1 _ Restek CLPesticides1
COL2 _ Restek CLPesticides2

Retention Times of Target Compounds with the following conditions:

Injector: 220°C
Detector: 305 °C
Carrier Gas Flow: Helium at ~2mL/min (per column) (pressure at 20psi, constant)
Make-up Gas Flow: Nitrogen at ~60mL/min (per detector)

Temperature program:

Initial Temp:	40 C
Initial Hold:	0.50 min
Program Rate 1	12 C/min
HoldTemp 1:	200 C (hold for 4 minutes)
Program Rate 2	30 C/min
FinalTemp :	305 C (hold for 2 minutes)
TOTAL TIME	22.50 minutes

APPENDIX B - Example Standard Preparation Recipes

Calibration Standard Volumes

STOCK STANDARD	CONC. (ug/mL)	1*	2*	3*	4*	5*	6*	7*
Dicamba, 2,4,5-TP (Silvex), 2,4,5-T 2,4-D, 2,4-DB, Dichlorprop Dinoseb MCPA, MCPP	10 100 50 10000	5	10	12.5	20	50	67	100

* microliters to 10mL hexane

Calibration Standard Concentrations

STOCK STANDARD	CONC. (ug/mL)	1*	2*	3*	4*	5*	6*	7*
Ultra HBM-8150M								
Dicamba, 2,4,5-TP (Silvex), 2,4,5-T	10	0.005	0.010	0.0125	0.020	0.050	0.067	0.10
2,4-D, 2,4-DB, Dichlorprop	100	0.050	0.10	0.125	0.20	0.50	0.67	1.0
Dinoseb	50	0.025	0.050	0.0625	0.10	0.25	0.33	0.50
MCPA, MCPP	10000	5.0	10	12.5	20	50	67	100

*ug/mL

APPENDIX B - Example Standard Preparation Recipes

HERBICIDE MOLECULAR WEIGHTS AND CORRECTION FACTORS

Herbicide acid	MWacid	MWester/ether	Correction factor
2,4-D	221.04	235.07	0.940
Dalapon	142.97	157.00	0.911
2,4-DB	249.09	263.12	0.947
Dicamba	221.04	235.07	0.940
Dichloroprop	235.07	249.09	0.944
Dinsoeb	240.22	254.24	0.945
MCPA	200.62	214.65	0.935
MCPP	214.65	228.67	0.939
2,4,5-TP(Silvex)	269.51	283.54	0.951
2,4,5-T	255.48	269.51	0.948
DCAA	205.04	219.07	0.936
Picloram	241.48	255.51	0.945
Pentachlorophenol	266.35	280.37	0.950

Example Calculation

$$CF(2,4-D) = \frac{Wacid}{Wester} = \frac{221.04}{235.07} = 0.94$$

If the standard is expressed as mass of ester per volume, convert the concentration to he acid form by multiplying by the correction factor (CF).

APPENDIX C – Method Summary

HOLD TIMES

MATRIX(method)	Chemical Preservative/ Storage*	Routine Container	Sample Hold Time	Extract Hold Time
Drinking water (515.1)	80mg sodium thiosulfate per liter; 4C	1-L amber x 2	14 days	28 days
Groundwater and Wasewater (615 and 8151)	None; 4C	1-L amber x 2	7 days	40 days
Soils and wastes (8151)	None; 4C	500-mL glass	14 days	40 days

*Storage temperature is 4C with control criteria of less than 6C with no frozen samples

EXTRACTION – detailed description in SOP EX45

Aqueous - adjust 500mL of sample to pH >12 and hydrolyze for one hour; extract with methylene chloride to remove non-targets and discard solvent; adjust aqueous phase to pH <=2 and extract with diethyl ether; concentrate, esterify and dilute to 10mL final volume with hexane

Soils - acidify 30g of sample, mix with acidified sodium sulfate; and sonicate with diethyl ether; hydrolyze with KOH at pH>12 and discard solvent; adjust aqueous phase pH to <=2 and extract with diethyl ether; concentrate, esterify, and dilute to final volume of 10mL with hexane.

ANALYSIS
Dual capillary columns with dual EC; 2-5uL injection into glass tee or y-splitter; external or internal standard calibration

SURROGATE(S):
DCAA - 0.25ug/L

BATCH QC
Method blank
LCS/LCSD- full target list of single peak analytes
MS/MSD- full target list of single peak analytes

Analytical Sequence

Method 515.1

Initial Calibration Standards
Initial Calibration Verification (ICV)
Laboratory Performance Solution (Daily)
Client samples analyzed until 12 hour clock expires
Calibration Verification standard – vary concentration
Client samples analyzed until 14 hour clock expires
Calibration Verification standard – vary concentration

Method 615

Initial Calibration Standards
Initial Calibration Verification (ICV)
Client samples analyzed until 24 hour clock expires
Calibration Verification standard – mid-level concentration
Client samples analyzed until 24 hour clock expires

Method 8151A

Initial Calibration Standards
Initial Calibration Verification (ICV)
20 client samples or 12 hours
Calibration Verification standard – mid-level concentration
20 client samples or 12 hours
Calibration Verification standard – mid-level concentration

The sequence continues until all samples have been analyzed or until the calibration verification fails the acceptance criteria. All sample extract analyses must be bracketed by acceptable verification standards if external standard calibration is used; if internal standard calibration is used, capping of the sequence by a CCV standard is not required unless specified in an agency or client QAPP. The default procedure is not to count the QC items in the 20 sample extracts that may be analyzed in the clock; i.e.; the number of sample and QC extracts may exceed 20 but the total number of sample extracts may not exceed 20 and all extracts (samples and QC) must be analyzed within the 12-hour clock.

Laboratory Performance Solution Criteria (515.1)

Test	Analyte(s)	Concentration (ug/mL)	Criteria
Sensitivity	Dinoseb	0.004	S/N >3
Chromatographic Performance	4-Nitrophenol	1.6	0.95<PGF<1.05
Column Performance	3,5-Dichlorobenzoic acid 4-Nitrophenol	0.6 1.6	Resolution >0.4

S/N = a ratio of peak signal to baseline noise.

peak signal - measured as height of peak.
baseline noise - measured as maximum deviation in baseline (in units of height) over a width equal to the width of the base of the peak.

PGF – Peak Gaussian factor b

$$PGF = \frac{1.83 \otimes W1}{W2}$$

where:
W1 = the peak width at half height in seconds
W2 = the peak width in seconds at one-tenth height (in seconds)

Resolution (R) between the two peaks as defined by the equation:

$$R = \frac{t}{Wavg}$$

where:
t = the difference in elution times between the two peaks
Wavg = the average peak width of the two peaks (measurements taken at baseline)

This is a measure of the degree of separation of two peaks under specific chromatographic conditions.

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Initial Calibration- 5-point minimum with lowest point at RL	Prior to sample analysis or when CCV fails	1) 515.1 %RSD of each target <=20% or r^2 >0.99 2) 615 %RSD of each target <=10% or r^2 >0.99 3) 8151 %RSD of each target <=20% or r^2 >0.99 (see Section 10.2 for 8000-series "grand mean" exception)	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and analyze standards
Initial calibration verification(ICV)	After Initial Calibration	515.1: Percent difference <=20% 615/8151: Percent difference <= 15%	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Laboratory Performance Check Solution	Daily, prior to sample analyses	See criteria above.	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance and reanalyze standards
Continuing calibration verification(CCV)	515.1/8151: After every twenty sample analyses (or 12 hours) and at the end of the sequence	515.1:Percent difference or drift <= 20% 615/8151: Percent difference or drift <= 15%	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze standard(s) -Remake and reanalyze standard(s) -Perform instrument or column maintenance

	615: After every twenty sample analyses (or 24 hours)	(see Section 10.3 for 8000-series"grand mean" exception)	and reanalyze standards
Method blank	Per batch	All targets reported less than RL in LQM	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze -Follow guidance in SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze
Lab control sample (LCS)	Per batch	Recoveries within LQM limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze -Follow guidance in SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze

QC CHECK	FREQUENCY	ACEPTANCE CRITERIA	CORRECTIVE ACTION
Matrix spike (MS) and matrix spike duplicate (MSD)	Per batch	Recoveries within LQM limits	-Evaluate chromatogram and integrations. Check calculations. - Follow guidance in SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze
Surrogate	All samples, method blanks, and QC	Recoveries within LQM limits	-Evaluate chromatogram and integrations. Check calculations. -Reanalyze - Follow guidance in SOP AN02 -Perform instrument or column maintenance, recalibrate, and reanalyze
Reporting limit (RL) standard - lowest level calibration standard	Daily - required for Fla DEP	Detected with reasonable sensitivity	-Reanalyze RL standard -Remake and reanalyze RL standard -Perform instrument or column maintenance, recalibrate, and reanalyze associated samples
Initial Demonstration of Capability (IDOC)	Initially and when new analysts trained	Evaluate in accordance with method criteria	Repeat test for analytes that fail criteria
Method Detection Limit (MDL)	See SOP CA90	Evaluate in accordance with SOP CA90	Evaluate in accordance with SOP CA90
Retention time window determination	See SOP AN66	See SOP AN66	See SOP AN66

SEVERN TRENT SERVICES

EXTRACTION OF CHLORINATED HERBICIDES IN WATERS, SOILS, AND WASTES

Methods: 8151A, 615, & 515.1

Approved by: R Wayne Robbins   26 April 2002
Date

Title: Technical Manager, QA

STL X Savannah ___ Tallahassee ___ Mobile ___ Tampa

1.0 SCOPE AND APPLICATION

This SOP describes the process for extracting chlorinated herbicides from aqueous samples, soils and sediments, and wastes.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Aqueous: A known volume of aqueous sample, nominally 500mL, is transferred to a Teflon separatory funnel. The sample is hydrolyzed with base to convert the herbicides to the salt form. The hydrolyzed sample is extracted with methylene chloride to remove the non-phenoxy acid herbicide material. The sample is acidified and extracted with diethyl ether. The extract is dried, filtered, concentrated, esterified with diazomethane, dissolved in hexane, and analyzed by GC/ECD.

2.2 Soils/Sediments: A known weight of a sample, approximately 30g wet weight, is acidified with hydrochloric acid (HCl) and combined with acidified sodium sulfate to form a free flowing, sandy mixture. Diethyl ether is added to the dried sample, and the sample is extracted using an ultrasonic disrupter for three minutes. The solvent is decanted and collected, and the extraction is repeated two more times with fresh portions of diethyl ether. The extract is transferred to a separatory funnel containing water that has been adjusted to pH>12. The sample is allowed to hydrolyze for one hour to convert the acid and ester forms of the herbicides to the salt forms. The solvent is discarded and the aqueous phase, which contains the herbicides in the salt form, is acidified and extracted with diethyl ether. The extract is dried, concentrated, esterified with diazomethane, dissolved in hexane, and analyzed by GC/ECD.

2.3 Waste: A known weight of waste, nominally 1.0g, is diluted to 10mL with diethyl ether. The extract is hydrolyzed with base and back-extracted with diethyl ether. The aqueous phase, which contains the herbicides in the salt form, is acidified and extracted with diethyl ether. The extract is dried, concentrated, esterified with diazomethane, dissolved in hexane, and analyzed by GC/ECD.

2.4 This procedure is based on SW-846 Method 8151A; however, the following modifications have been made to the procedure:

Diethyl ether is used as the extraction solvent for soils in place of 1:1 acetone/methylene chloride. This step was modified to improve recovery of chlorinated herbicides. Recoveries of the herbicides using acetone/methylene chloride were found to be less than 10%.

The initial extract of soils is not concentrated prior to hydrolysis. The entire extract is transferred to a separatory funnel containing water that has been adjusted to pH >=12 for hydrolysis.

3.0 SAFETY

3.1 Use good common sense when working in the lab. Do not perform any procedures that you do not understand or that will put you or others in potentially dangerous situations.

3.2 This SOP contains procedures that are designed to reduce the exposure of lab personnel to solvent vapors and to minimize the amount of solvent introduced into the lab air. All solvent transfer steps should be performed quickly and under a hood, if possible. Use the minimum amount of solvent to get the job done. Do not allow open containers of solvents or extracts to evaporate into the lab.

3.3 A lab coat or apron should be worn to protect clothing and skin from acids, bases, and solvents. Gloves must be worn to protect hands, and eye protection (safety glasses, goggles) must be worn at all times in the lab. An analyst should not work alone in an isolated area.

3.4 Diethyl ether is a flammable solvent that can cause drowsiness. The extraction analyst using diethyl ether must not work alone in an isolated area of the lab. A solvent such as diethyl ether can cause a burning sensation when it contacts the skin. The rapid evaporation of the solvent causes a rapid heat loss in the skin, which is similar to frost bite. If this occurs, rinse the exposed skin in cold water to reduce the solvent evaporation.

3.5 The lab should keep only the minimum supply of diethyl ether. Diethyl ether will form explosive peroxides if stored in the lab for long periods of time. Opened containers of diethyl ether should be checked periodically for peroxides using peroxide test strips.

3.6 The analyst should become familiar with the Material Safety Data Sheets (MSDS) for each reagent and standard used in this procedure. The MSDS denote the type of hazard that each reagent poses and the safe handling instructions for these compounds.

4.0 INTERFERENCES

4.1 Improperly cleaned glassware can contribute interferences to the sample extract. Material that is left inside the extraction vessels and glassware after cleaning may show up in the next extraction. The glassware must be properly cleaned according to SOP AN60: *Glassware Cleaning Procedures.*

4.2 Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion or may be "salted out" by the addition of sodium chloride.

4.3 The glassware used for herbicides should not be used to extract or concentrate dioxins and furans. Several of the herbicides are precursors to the formation of dioxins or are associated with the presence of dioxins in the environment.

4.4 The base hydrolysis step removes interferences from the sample extract. Dinoseb, a phenolic herbicide, is very reactive and will have poor recoveries when subjected to the base hydrolysis step.

5.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

5.1 Aqueous samples are routinely collected in 1-L amber glass containers fitted with Teflon-lined caps. No preservative is required. The sample is iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab. Samples must be extracted within seven days of collection and the extract must be analyzed within forty days of extraction.

TCLP leachate samples are stored in the same manner as aqueous field samples. The extraction must be performed within seven days of the leaching procedure and the extract analyzed within forty days of extraction.

5.2 Soils, sediments, sludges, and wastes are collected in glass containers fitted with Teflon-lined caps. The routine container is 500-mL glass. Larger or smaller containers may be supplied. No preservative is required. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen samples) in the lab. The hold time for herbicides in solid and non-aqueous matrices is 14 days from the date of collection. The extract must be analyzed within forty days of extraction.

6.0 APPARATUS AND MATERIALS

6.1 Separatory funnels - 1-L and 2-L, Teflon with Teflon stopcocks. Glass funnels may also be used.

6.2 Large funnels

6.3 Pyrex glass wool – rinse with acidified methanol prior to use.

6.4 Disposable, glass volumetric pipettes

6.5 Stainless steel spatulas

6.6 Wide range and narrow range pH paper

6.7 Pre-cleaned 500-mL extraction bottles. Discard after use.

6.8 1-L pre-cleaned containers. This is the same container used to collect the sample and can be used to collect the aqueous phase during the solvent wash. Discard after use.

6.9 Ultrasonic disrupter - Tekmar Model or equivalent with horn-type titanium-tipped sonication probe. The sonicator should be capable of operating in the pulse mode at full power.

6.10 Sonabox - the sonicator should be placed in the sonabox to reduce noise. The sonabox must be placed under a fume hood.

6.11 Filter paper - grade 414, 18.5cm diameter

6.12 Top-loading balance - capable of weighing to 0.1g. The balance calibration must be verified according to SOP AN10: *Balance Calibration and Use* each time the balance is used.

6.13 12mL vials with Teflon-lined caps.

6.14 Diazomethane generator.

NOTE: If the herbicide blank is contaminated, clean the generator tubing and vessels with methylene chloride, methanol, and diethyl ether, in that order, and purge the apparatus with nitrogen to dry. Replace the Teflon tubing and vessels if the solvent cleaning does not improve the blank.

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44: *Reagent Traceability.*

7.1 Reagent water - lab generated deionized water

7.2 Sodium sulfate, powdered and granular, anhydrous - purified by heating at 400C for four hours in a shallow tray

7.3 Acidified sodium sulfate - Transfer purified sodium sulfate to a suitable glass container until the container is about ¾ full. Working under a hood, add enough diethyl ether to wet the sodium sulfate. Add 1-2mL of concentrated sulfuric acid for each kilogram of sodium sulfate and stir to mix the acid into the solvent and sodium sulfate. Add more diethyl ether to keep the sodium sulfate wet while stirring the sodium sulfate. The acid must be thoroughly mixed into the sodium sulfate and diethyl ether. Pour off the excess solvent and allow the diethyl ether to evaporate under a hood for 24 hours. Store in a glass container. Check the pH of the acidified sodium sulfate by mixing 1g and 5mL of water in a small container. The pH of the solution should be less than 4.

7.4 Methanol - residue grade or better

7.5 Diethyl ether - residue grade or better. Check periodically for formation of peroxides.

7.6 Sodium hydroxide (NaOH) - reagent grade

7.7 Sodium hydroxide solution (10N) - Dissolve 400g of NaOH pellets into about 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the NaOH in small portions, with constant stirring, to minimize the time it takes to dissolve the pellets. A good deal of heat will be generated as the NaOH dissolves. After all 400g has been added, carefully dilute to 1000mL with reagent water. Mix the solution thoroughly and transfer to a storage container. Do not store sodium hydroxide solution in volumetric glassware or in containers with ground glass joints.

7.8 Sulfuric acid (H_2SO_4) - concentrated reagent grade

7.9 Sulfuric acid solution (1:1 v/v) - Slowly and carefully add 500mL of concentrated H_2SO_4 to 500mL of reagent water contained in a 2-L beaker on a magnetic stirrer. Add the acid in small portions with constant stirring to reduce the heat evolved when the acid and water are combined. Cool and transfer the solution to a labeled storage container.

7.10 Hydrochloric acid (HCl) - concentrated, reagent grade

7.11 Potassium hydroxide (KOH) - reagent grade

7.12 Potassium hydroxide solution (37%) - Weigh 3g of KOH into a 100mL volumetric flask and dilute to volume with reagent water.

7.13 Acidified methanol (approximately 0.12N) - Carefully add 5mL of concentrated HCl to 400mL of methanol in a 500mL volumetric flask. Dilute to volume with methanol. Larger volumes may be prepared.

7.14 Diazald (N-methyl-N-nitroso-toluenesulfonamide) - reagent grade

7.15 Carbitol - reagent grade or better

7.16 Silicic acid – reagent grade

7.17 Hexane - residue grade or better

7.18 Sodium chloride - reagent grade, purified, if necessary, by Soxhlet extraction with methylene chloride or by heating at 400C for four hours in a shallow tray

8.0 STANDARDS

The preparation of the spiking solutions must be tracked in accordance with SOP AN41: *Standard Material Traceability.* General guidance on the preparation of standards is given in SOP AN43: *Standard Preparation.*

The lab should purchase certified solutions from STL-approved vendors, if available. The lab should prepare standards from neat materials only if a certified solution is not available.

The following "recipes" provide guidance for the preparation of the surrogate and matrix spiking solutions:

8.1 Preparation of the Herbicide Surrogate Spiking Solution

8151 Surrogate Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (mL)	*Vspike* (mL)	*Cspike* (ug/mL)
DCAA	100	1.0	50	2.0

Solvent: Methanol

8.2 Preparation of the Herbicide Matrix Spiking Solutions

8151 Matrix Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (mL)	*Vspike* (mL)	*Cspike* (ug/mL)
Chlorinated Herbicides Mixture	100	0.50	50	1.0

Solvent: Methanol

8151 TCLP Matrix Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (mL)	*Vspike* (mL)	*Cspike* (ug/mL)
Herbicide TCLP Mix	2000	0.025	50	1.0

Solvent: Methanol

8151 Full Target Matrix Spiking Solution

Stock Standards	*Cstock* (ug/mL)	*Vstock* (uL)	*Vspike* (mL)	*Cspike* (ug/mL)
Chlorinated Herbicides Mixture: Dicamba, Silvex, 2,4,5-T Dinoseb, 2,4-D, Dichorprop, 2,4-DB, Dalapon, and	200	50	10	1.0
MCPA, MCPP	20,000			100

Solvent: Methanol

9.0 SAMPLE PREPARATION

The samples and QC items must be clearly and unambiguously labeled during each step of the extraction and analysis process. Labeling tape should be used to identify the glassware associated with each sample. Solvents will erase grease pens and "Sharpies." Use of different colored labeling tape will aid the analyst in keeping up the extracts during each step of the extraction and concentration process.

9.1 Extraction of Aqueous Samples and TCLP Leachates

9.1.1 Remove the samples from the storage refrigerator and allow the samples to come to room temperature. Begin filling out the extraction log and gathering the required glassware while the samples are warming up. The glassware should be rinsed with acidified methanol and then with diethyl ether prior to extraction.

NOTE: All glassware used in this procedure must be rinsed with acidified methanol and diethyl ether prior to use.

9.1.2 Inspect the samples. Determine if the samples have multiple layers such as a sediment or an oil layer. Samples with large amounts of sediments or particulates may clog the stopcock on the separatory funnel. Consult with the supervisor or technical manager if the sample matrix is unusual or is difficult to categorize. Any unusual sample preparation steps required prior to the extraction must be noted on the extraction log or in an anomaly report.

9.1.3 Thoroughly mix the sample by inverting the container several times and pour 500mL of the sample into a graduated cylinder that has been rinsed with acidified methanol. Transfer the sample to a properly labeled 1-L or 2-L Teflon separatory funnel. For TCLP samples, transfer 10mL of the leachate to a separatory funnel and dilute to 500mL with reagent water.

Transfer two additional 500mL aliquots of the sample selected for the MS and MSD to labeled separatory funnels.

9.1.4 Add 500mL of reagent water to each of two separatory funnels to serve as the method blank and laboratory control spike (LCS).

9.1.5 Add 1.0mL of surrogate to each sample, method blank, laboratory control spike, and matrix spike.

9.1.6 Add 1.0mL of matrix spiking solution to all appropriate lab control spikes and matrix spikes.

NOTE: Every extraction batch of 20 or fewer samples will have a method blank and a laboratory control spike (LCS). A matrix spike (MS) and a matrix spike duplicate (MSD) are prepared at a frequency of 5% of samples (one MS and one MSD per 20 samples) or as required by contract or client QAP. If insufficient sample is available for the MS/MSD, the extraction log must be stamped: " Insufficient sample is available to perform the MS/MSD".

9.1.7 Add 100g of sodium chloride to each sample and QC item as needed.

9.1.8 Adjust the pH of the sample to >12 with 10N NaOH. Check the pH with narrow range pH paper. Allow the samples to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

NOTE: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are extracted out of the sample with methylene chloride. The rest of the extraction steps may be performed with manual or automatic shaking.

9.1.9 Add 50mL of methylene chloride to each separatory funnel.

9.1.10 Shake each separatory funnel for three minutes with periodic venting to release any excess pressure. If an automatic shaker is used, shake the samples for ten minutes. Allow ten minutes for complete separation between the lower solvent and upper water phases.

NOTE: The separatory funnel should be vented under a hood to remove the solvent fumes from the lab.

9.1.11 Drain the lower layer (methylene chloride) into a designated waste container.

NOTE: Samples with high levels of organic material (oils, particulates, etc.) may cause the formation of emulsions during the extraction. Emulsions will occur most readily during the "base shake" to remove the non-target compounds. The extract may be filtered or stirred to remove the emulsion. Small aliquots of sodium sulfate may also be gently added to the extract to remove the emulsion.

9.1.12 Repeat Steps 9.1.9 through 9.1.11 two more times, discarding the methylene chloride layer (lower layer) each time.

9.1.12 Adjust the pH of each of the samples and QC items to <2 with cold 1:1 sulfuric acid. Add the acid slowly and gently swirl the separatory funnels to ensure that the acid and base have reacted. Acid/base neutralization reactions can be violent if mixed too quickly. Check the pH of the samples and QC items to ensure that the pH < 2.

9.1.13 Add 150mL of diethyl ether to each sample and QC item.

-If performing a "manual shake", shake the funnels for one minute, venting frequently to release any pressure.

-If using the automatic shaker, shake the samples continuously for ten minutes, releasing the pressure periodically.

9.1.14 After the extraction, allow the layers to separate for at least ten minutes. Collect the water layer (lower layer) in a large beaker or flask that has been rinsed with acidified methanol and diethyl ether.

9.1.15 Collect the extract (upper layer) into a 500-mL pre-cleaned extraction bottle containing 30g acidified sodium sulfate.

9.1.16 Pour the samples back into their respective separatory funnels and check the pH. Adjust to <2 with 1:1 sulfuric acid if the pH is >2.

9.1.17 Repeat the extraction in Steps 9.1.13 through 9.1.16 two more times with fresh 50mL aliquots of diethyl ether. Combine the extracts from the three extractions in the respective bottles containing the acidified sodium sulfate. Discard the water layer. Allow the extract and sodium sulfate to remain in contact at least two hours but preferably overnight. (This is a good stopping point.)

9.1.18 Place a piece of filter paper into a glass funnel and add a small amount of acidified sodium sulfate. Filter the extract through the glass funnel and collect the extract directly into a labeled K-D apparatus. Break up any sodium sulfate that has solidified with a glass rod. Rinse the flask with a small portion of diethyl ether, filter, and collect. It is important that the extract be dried thoroughly.

9.1.19 Concentrate the extract to a final volume of approximately 10mL. The extract may be left in the 10mL graduated concentrator tube or transferred to a labeled storage vial. The extract is now ready for the diazomethane esterification.

9.2 Extraction of Soils and Solids

9.2.1 Remove samples to be extracted from the storage refrigerator and allow the samples to come to room temperature while the extraction glassware is being prepared. Begin filling out the extraction log and gathering the required glassware while the samples are warming up. The glassware should be rinsed with acidified methanol and then with diethyl ether prior to extraction.

Check the "tune" of the sonicator using the procedure in SOP AN15: *Tekmar Sonic Dismembrator Tuning Procedure*.

9.2.2 Collect the appropriate glassware and rinse with acidified methanol and diethyl ether prior to use.

9.2.3 Prepare the funnels to filter the extracts by placing a piece of folded filter paper into the funnel. Rinse with acidified methanol and discard the solvent.

NOTE: Record as much information on the extraction log as possible before beginning the extraction to minimize the number of entries required during the extraction.

9.2.4 Open the sample container and inspect the sample. Note any unusual characteristics such as the presence of rocks, sticks, leaves, or other materials. Thoroughly homogenize the sample, mixing in any water that may be present on top of the sediment or soil. SOP AN70: *Homogenization and Compositing of Field Samples and Segregation of High Concentration Volatile and Semivolatile Samples* gives guidance for homogenization of samples.

NOTE: If it is difficult to homogenize the sample or if the sample matrix is difficult to characterize, contact the supervisor before proceeding with the extraction. A careful inspection of the sample at this point can save time and effort later on in the analysis. Any unusual sample preparation steps required prior to the extraction must be noted on the extraction log or in an anomaly report.

9.2.5 Weigh 30.0-30.5g of the homogenized sample into a pre-cleaned, labeled 500-mL extraction bottle. Record the weight for all samples in this batch.

9.2.6 Weight 30g of acidified sodium sulfate into two separate beakers to serve as the method blank and laboratory control sample (LCS).

9.2.7 Weigh two additional 30.0-30.5g portions of the sample selected as the matrix spike (MS) and matrix spike duplicate (MSD).

NOTE: Each extraction batch of twenty or fewer samples will have the following QC items: method blank and LCS. MS and MSD are prepared at a frequency of 5% of samples (one MS and one MSD per 20 samples). If there is not enough sample to perform the MS/MSD, the extraction log must be stamped "Insufficient sample is available to perform the MS/MSD."

9.2.8 Working under a hood, acidify each sample and QC item with 0.1 to 0.2mL of concentrated hydrochloric acid. Add the acid to the sample slowly and carefully, stirring the sample with a stainless steel spatula, glass rod, or pipette. Continue to add acid until the pH <2 when read with narrow range pH paper.

9.2.9 Add acidified sodium sulfate to each sample and QC item. Stir with a glass rod or stainless steel spatula to form a sandy, free-flowing mixture. The sodium sulfate combines with the water in the sample to "dry" the sample (remove the water). More sodium sulfate may be required if the sample is very wet. Proceed to the next step as quickly as possible.

9.2.10 Add 1.0mL of the herbicide surrogate spiking solution to the method blank, LCS, MS, MSD, and each sample in the batch.

9.2.11 Add 1.0mL of the appropriate herbicide matrix spiking solution to the LCS, MS, and MSD. Transfer the extraction bottles to a hood near the sonicator.

9.2.12 Under a hood, add 100mL of diethyl ether to each sample and QC item. Stir the sample to break up any lumps that may have formed. Add more solvent until the solids are covered by about one inch.

9.2.13 Place the tip of the sonicator horn in the center of the beaker about ½ inch below the surface of the solvent but above the solid portion.

9.2.14 Sonicate for three minutes with the output control knob set at 10, mode switch to pulse, and percent duty cycle set at 50% If the sonication is properly performed, the solids and solvent will vigorously mix each time the sonicator pulses.

9.2.15 Under a hood, decant the extract through the filter funnel and collect the extract directly into a labeled, pre-cleaned 500-mL extraction bottle or Erlenmeyer flask.

9.2.16 Repeat the extraction two more times with fresh portions of solvent, collecting the solvent in the 500-mL bottle each time.

NOTE: Clean the sonicator horn between samples by rinsing with diethyl ether.

9.2.17 Add 500mL of reagent water to a 2-L Teflon separatory funnel. Adjust the pH of the water to pH >=12 using 10N KOH. Transfer the entire extract to the separatory funnel, using several small aliquots of diethyl ether to rinse the bottle.

Check the pH with narrow range pH paper. Allow the sample to stand for at least one hour with intermittent shaking or shake on the automatic shaker for one hour.

Check the pH again after the one hour time period. If the pH <12, adjust the pH to >= 12 and allow to stand or shake for an additional hour. The pH must remain at or above 12 during the hydrolysis step.

NOTE: This step is necessary to convert the acid and ester forms of the herbicides to the water-soluble salts. After the hydrolysis step, the non-target compounds are contained in the diethyl ether layer.

Discard the diethyl ether layer and retain the water layer for additional preparation steps. The rest of the extraction steps may be performed with manual or automatic shaking. The sample extraction/preparation steps from this point forward are the same as described in Sections 9.1.12 through 9.1.19.

9.3 Esterification with Diazomethane

9.3.1 If the final volume of the extract is not at 1mL, concentrate the extracts to approximately 1mL under a gentle stream of nitrogen.

9.3.2 After all of the extracts have been concentrated, prepare the diazomethane generation device for the esterification. Inspect the lines to ensure that there are no leaks or broken connections.

9.3.3 Place the extracts on the support. Replace all of the needles and place the needles into the first extracts to be esterified.

9.3.4 Add diethyl ether to the first container on the diazomethane generation device until the container is about ¾ full.

9.3.5 Add the following to the second container to esterify approximately 20 samples.

50mL diethyl ether
50mL 37% potassium hydroxide
50mL Carbitol
5g Diazald

NOTE: Smaller volumes and weights of reagents may be used if the ratios above are maintained.

Quickly attach the container to the diazomethane device and start the nitrogen flow. Recall that the needles should already be placed in the samples that are to be esterified first. The gas flow should be steady but not so high that the sample is bubbled out of the concentrator tube or that the sample is evaporated before the esterification can take place.

9.3.6 Allow the diazomethane to flow through the sample extracts until a persistent yellow color remains. This will usually take two to three minutes. The esterification process will take longer as the diazomethane is exhausted.

NOTE: For dark extracts where the persistent yellow color cannot be distinguished, esterify the samples for 10 minutes.

9.3.7 After the persistent yellow color remains, remove the needle from the tube in that position and replace it with a new needle. Place the needle into the next sample to esterify. Repeat for all samples in the batch, replacing the needle for each new extract. If a yellow color cannot be formed in a clear extract, the diazomethane has most likely been exhausted. Pour the used reagents into a waste container (under a hood) and replenish the reagents in the second container. Add more diethyl ether to the first container if needed.

9.3.8 After all of extracts have been esterified, add a small amount (about 0.1g) of silicic acid to each sample extract, cover the concentrator tubes with aluminum foil and allow the extracts to sit for 30 minutes. The silicic acid will destroy any unreacted diazomethane. Dilute to 10mL with hexane and transfer the extract to a labeled storage vial. Store the extracts at 4C until the time of analysis.

10.0 ANALYTICAL PROCEDURE

No items in this revision. The analytical procedure is described in SOP SG65: *Chlorinated Herbicides.*

11.0 CALCULATIONS

No items in this revision.

12.0 QUALITY CONTROL/QUALITY ASSURANCE

12.1 The analytical batch consists of up to twenty (20) client samples and the associated quality control items. The quality control items consist of a method (reagent) blank, a lab control standard (LCS), a matrix spike (MS), and a matrix spike duplicate (MSD). If insufficient sample is available for the MS/MSD, the LCS is prepared in duplicate.

SOP AN02: *Analytical Batching* contains guidance for evaluating the QC in an analytical batch.

12.2 The lab must perform a method detection limit (MDL) study annually in each matrix in accordance with SOP CA90: *Procedure for the Determination of Method Detection Limit (MDL).*

12.0 PREVENTIVE MAINTENANCE AND TROUBLESHOOTING

No items in this revision.

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

Excess samples, extracts, and reagents must be disposed in accordance with SOP CA70: *Waste Management.*

15.0 REFERENCES

Test Methods for Evaluating Solid Waste, Third Edition, SW-846; vs. EPA Office of Solid Waste and Emergency Response: Washington, DC. (Including Update III)

POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS (SW-846 Method 8280)

Approved by:

R. Wagerfield 6 Feb 2001
Date

Title: Technical Manager, QA

STL X Savannah __ Tallahassee __ Mobile __ Tampa

1.0 SCOPE AND APPLICATION

1.1 This method is used to determine the concentrations of chlorinated dibenzodioxins and chlorinated dibenzofurans in a variety of matrices. This SOP does not provide for the identification and quantitation of individual congener in these two classes of compounds, commonly referred to as dioxins and furans. 2,3,7,8-tetrachlorodibenzo-p-dioxin is the only congener that is identified and quantified. All other congeners and isomers are reported as groups and quantified against a 2,3,7,8-substituted isomer of that group.

1.2 The method detection limit (MDL), the reporting limits (RL), and the accuracy and precision criteria is given in the laboratory Quality Manual prepared by and for STL Savannah, STL Tallahassee, STL Mobile, and STL Tampa West.

2.0 SUMMARY OF METHOD AND DEFINITIONS

2.1 Samples are extracted according to their particular matrix type. The extract is subjected to an acid and base clean-up, alumina column cleanup, and the carbon column cleanup. The extract is taken to near dryness and recovered to a final volume of 200uL. A 2-uL aliquot of the extract is injected into a capillary column connected to a mass spectrometer(MS). The MS is set to run in the SIM (selected ion monitoring) mode. Quantitation is based on internal standard calibration.

2.2 This method is based on the SW-846 Method 8280 and 40 CFR Part 136 Method 613.

NOTE: This SOP is based on SW-846 Method 8280 and not on the newer revision of the method, 8280A.

3.0 SAFETY

3.1 Do not perform any procedures that you do not understand or that will put you or others in potentially hazardous situations.

CAUTION: Extreme care must be exercised when dealing with chlorinated dioxins and furans and samples containing these compounds. These compounds are thought to be carcinogenic at very low concentrations.

3.2 The splitless vent of the GC and the roughing pump on the mass spectrometer must be connected to a carbon trap. These traps must be changed frequently and the spent carbon disposed of in a manner consistent with dioxin/furan contamination.

3.3 This extraction procedure calls for cleanup of the extract using both acid and base. The extraction analyst must be aware of the danger of working with strong acid and base solutions. The extraction analyst must wear clothing that will protect him from these hazards - a lab coat or apron, eye protection, and latex gloves.

3.4 The Material Safety Data Sheets (MSDS) for each analyte and reagent used in this procedure is on file in the lab. The extraction analyst and the GC/MS analyst must be aware of the potential hazard that each material poses and the safe handling procedures that should be employed.

4.0 INTERFERENCES

4.1 Interferences can come from a variety of sources: glassware, reagents, solvents, and co-extracted contaminants. Glassware must be thoroughly cleaned with soap and water and then be rinsed with acetone, methylene chloride, and hexane to remove all traces of organic contamination.

4.2 Reagents and solvents must be of the highest purity and tested for contamination by the analysis of solvent, reagent, and method blanks. Co-extracted interferences are the greatest problem. The acid and base cleanup will remove many of the interferences from the extract.

4.3 Two column cleanup procedures are included in this SOP. The alumina column cleanup is not very effective on petroleum based contamination. The carbon column is based on the planar geometry of the PCDDs and PCDFs.

NOTE: Care should be taken to prevent any carbon fine from passing into the extract during the carbon column cleanup.

5.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

5.1 Aqueous Samples

Samples are collected in 1-L or 1-quart amber glass containers fitted with Teflon-lined caps. No chemical preservative is required. Samples are iced at the time of collection and stored in the laboratory at 4C (less than 6C with no frozen samples) until time of extraction. Aqueous samples for Method 8280 must be extracted within 30 days and analyzed within 45 days of collection. Method 613 requires that samples are extracted within 7 days of collection and analyzed within 40 days of extraction.

CAUTION: Protective clothing, gloves, and eye protection should be worn when handling standards and samples containing chlorinated dioxins and furans. Standards should be prepared in a glove box equipped with forced air filters.

5.2 Soil/Sediment and Waste Samples

Soil/sediment and waste samples should be collected in glass containers equipped with Teflon-lined caps. The samples are iced at the time of collection and stored at 4C (less than 6C with no frozen liquid samples) until time of extraction. Soil/sediment and waste samples must be extracted within 30 days of collection and analyzed within 45 days of collection for method 8280.

CAUTION: Protective clothing, gloves, and eye protection should be worn when handling standards and samples containing chlorinated dioxins and furans. ~~Standards should be prepared in a glove box equipped with forced air filters.~~

6.0 APPARATUS AND MATERIALS

6.1 Gas chromatograph, HP 5890 or equivalent instrument equipped with a split/splitless injector

6.2 Mass spectrometer, HP 5970 (MSD) or equivalent instrument

6.3 Capillary column, DB-5MS, 30 m x 0.25 mm i.d., 0.5 um film

6.4 Syringes: 10-, 25-, 50-, 100-mL

6.5 Volumetric flasks: 1-, 10-, 50-, 100-mL

6.6 Disposable glass pipets: 1-, 2-, 10-mL

6.7 Autosampler vials: 2mL with crimp tops and 250uL inserts

6.8 Continuous liquid-liquid extraction bodies

6.9 Zymark concentrating apparatus

6.10 Screw top vials: 20-, 40-mL

6.11 Separatory funnels: 2000-mL, 250-mL

6.12 Beakers: 600-mL glass

6.13 Receiving tube:10-mL

6.14 Snyder column: 3-ball

6.15 Wrist-action shaker

7.0 REAGENTS

Reagents must be tracked in accordance with SOP AN44:*Reagent Traceability*.

7.1 Methylene chloride - Burdick and Jackson pesticide grade or GC2 grade.

7.2 Hexane-Burdick and Jackson pesticide grade or GC2 grade.

7.3 Acetone-Burdick and Jackson pesticide grade or GC2 grade.

7.4 Toluene-Burdick and Jackson pesticide grade or GC2 grade

7.5 Methanol-Burdick and Jackson pesticide grade or GC2 grade

7.6 Petroleum ether-Burdick and Jackson pesticide or GC2 grade

7.7 Sodium sulfate (Na_2SO_4): heated in muffle furnace for 4 h at 500C.

7.8 Potassium hydroxide (KOH)-reagent grade

7.9 Potassium hydroxide solution, 20%: Slowly add 200g of reagent grade KOH to 800mL of reagent water. Dissolve and dilute to 1L.

7.10 Sulfuric acid: Concentrated-Mallinkrodt.

7.11 Sodium chloride (NaCl) - reagent grade

7.12 Sodium chloride solution (5% w/v): Add 50g of reagent grade sodium chloride to a 1-L volumetric flask. Add enough reagent water to dissolve the salt and dilute to 1L with reagent water. Mix well and transfer to a 1-L container.

7.13 Reagent water - lab generated deionized water or other source that is free of contamination and interferences.

8.0 STANDARDS

Standards must be tracked in accordance with SOP AN41:*Standard Material Traceability.*

8.1 Window Defining Mix Standard
A solution containing the first and last eluting dioxin and furan congeners of each level of chlorination (first and last tetra; first and last penta, etc.) must be purchased. Sources of this mixture include Wellington Laboratories and Cambridge Isotopes.

8.2 Calibration Standards

8.2.1 The primary stock standards are purchased as certified solutions from vendors. The primary stock standards used in this procedure are listed in Table 3 of this SOP.

8.2.2 All primary (1E) stock standards are purchased from vendors. Secondary (2E) (or intermediate) standard solutions are made from the primary stock standards. The following table illustrates the preparation of (2E) standards from the primary stock standards.

Standard	**Components**	**C_i**	**Amount Component**	**V_f**	**C_f**
(2E) 2,3,7,8 T-HCDD/F	(1E) 2,3,7,8 T-HCDD H_pCDD (1E) 2,3,7,8 T-HCDF H_pCDF	25,000 ng/mL 25,000 ng/mL	500 µL 500 µL	5mL (Hexane)	2,500 ng/mL
(2E) 1,2,3,4,6,7,8,9 OCDD/F	(1E) 1,2,3,4,6,7,8,9 OCDD (1E) 1,2,3,4,6,7,8,9 OCDF	10,000 ng/mL 50,000 ng/mL	1,250 µL 250 µL	5mL (Hexane)	2,500 ng/mL

8.2.3 Calibration Standards are prepared at six levels of concentrations: 25ng/mL A(O); 50ng/mL B(1); 75ng/mL C(2); 100ng/mL D(3); 150ng/mL E(4); and 250ng/mL F(5) from (2E) and (1E) stock standards.

Standard	Components	C_i	Amount Component	V_f	C_f
Cal Stand. A (0)	(2E) T-H_pCDD/F (2,3,7,8) (2E) OCDD/F (1,2,3,4,6,7,8,9) (1E) 1,2,3,4 TCDD $^{13}C_6$ (1E) 2,3,7,8 TCDD $^{13}C_{12}$ (1E) 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$	2,500 ng/mL 2,500 ng/mL 50,000 ng/mL 50,000 ng/mL 10,000 ng/mL	10 µL 10 µL 10 µL 10 µL 50 µL	1mL (Nonane)	25 ng/mL ISTD and recovery std. at 500 ng/mL
Cal Stand. B (1)	(2E) T-H_pCDD/F (2,3,7,8) (2E) OCDD/F (1,2,3,4,6,7,8,9) (1E) 1,2,3,4 TCDD $^{13}C_6$ (1E) 2,3,7,8 TCDD $^{13}C_{12}$ (1E) 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$	2,500 ng/mL 2,500 ng/mL 50,000 ng/mL 50,000 ng/mL 10,000 ng/mL	20 µL 20 µL 10 µL 10 µL 50 µL	1mL (Nonane)	50 ng/mL ISTD and recovery std. at 500 ng/mL
Cal Stand. C (2)	(2E) T-H_pCDD/F (2,3,7,8) (2E) OCDD/F (1,2,3,4,6,7,8,9) (1E) 1,2,3,4 TCDD $^{13}C_6$ (1E) 2,3,7,8 TCDD $^{13}C_{12}$ (1E) 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$	2,500 ng/mL 2,500 ng/mL 50,000 ng/mL 50,000 ng/mL 10,000 ng/mL	30 µL 30 µL 10 µL 10 µL 50 µL	1mL (Nonane)	75 ng/mL ISTD and recovery std. at 500 ng/mL
Cal. Standard D (3)	(2E) T-H_pCDD/F (2,3,7,8) (2E) OCDD/F (1,2,3,4,6,7,8,9) (1E) 1,2,3,4 TCDD $^{13}C_6$ (1E) 2,3,7,8 TCDD $^{13}C_{12}$ (1E) 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$	2,500 ng/mL 2,500 ng/mL 50,000 ng/mL 50,000 ng/mL 10,000 ng/mL	40 µL 40 µL 10 µL 10 µL 50 µL	1mL (Nonane)	100 ng/mL ISTD and recovery std. at 500 ng/mL
Cal. Standard E (4)	(2E) T-H_pCDD/F (2,3,7,8) (2E) OCDD/F (1,2,3,4,6,7,8,9) (1E) 1,2,3,4 TCDD $^{13}C_6$ (1E) 2,3,7,8 TCDD $^{13}C_{12}$ (1E) 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$	2,500 ng/mL 2,500 ng/mL 50,000 ng/mL 50,000 ng/mL 10,000 ng/mL	60 µL 60 µL 10 µL 10 µL 50 µL	1mL (Nonane)	150 ng/mL ISTD and recovery std. at 500 ng/mL
Cal. Standard F (5)	(2E) T-H_pCDD/F (2,3,7,8) (2E) OCDD/F (1,2,3,4,6,7,8,9) (1E) 1,2,3,4 TCDD $^{13}C_6$ (1E) 2,3,7,8 TCDD $^{13}C_{12}$ (1E) 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$	2,500 ng/mL 2,500 ng/mL 50,000 ng/mL 50,000 ng/mL 10,000 ng/mL	100 µL 100 µL 10 µL 10 µL 50 µL	1mL (Nonane)	250 ng/mL ISTD and recovery std. at 500 ng/mL

(2E) 1,2,3,4 TCDD is added only to Standard C. Standard C is usually made @ 5mL final volume.

8.3 Internal Standards/Matrix Spike

Internal standard spikes (ISTD) A and B (2,3,7,8 TCDD $^{13}C_{12}$ and 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$, respectively) are prepared from (1E) stock standards to a final concentration of 100 ng/mL. 2,3,7,8 T-HCDDD/F and 1,2,3,4,6,7,8,9 OCDD/F matrix spike solutions are prepared from (1E) stock standards to a final concentration of 25 ng/mL. The preparation for internal standards and matrix spike is as follows:

Standard	Components	C_i	Amount Component	V_f	C_f
ISTD A	(1E) 2,3,7,8 TCDD $^{13}C_{12}$	50,000 ng/mL	200 µL	100mL (Acetone)	100 ng/mL
ISTD B	(1E) 1,2,3,4,6,7,8,9 OCDD $^{13}C_{12}$	10,000 ng/mL	1000 µL	100mL (Acetone)	100 ng/mL
T-H_pCDD/F Matrix Spike	(1E) 2,3,7,8 T-H_pCDD (1E) 2,3,7,8 T-H_pCDF	25,000 ng/mL 25,000 ng/mL	50 µL 50 µL	50mL (Acetone)	25 ng/mL
OCDD/F Matrix Spike	(1E) 1,2,3,4,6,7,8,9 OCDD (1E) 1,2,3,4,6,7,8,9 OCDF	10,000 ng/mL 50,000 ng/mL	125 µL 25 µL	50mL (Acetone)	25 ng/mL

8.4 Recovery Standard Solution

Recovery standard, 1,2,3,4-TCDD $^{13}C_6$, is also made up from a (1E) stock standard. The final concentration of this standard is 500 ng/ml. The preparation for recovery standard is as follows:

Standard	Components	C_i	Amount Component	V_f	C_f
Recovery Standard	(1E) 1,2,3,4 TCDD $^{13}C_6$	50,000 ng/mL	500 µL	50 (Nonane)	500 ng/mL

8.5 Assay Preparation

Prior to the use of any internal standard, matrix spike, or recovery standard solutions, an aliquot of the solution should be analyzed to ensure that the solutions were made correctly. Assay are prepared as follows:

Internal Standard A/B	100ul of Internal Standard + 100ul Recovery Standard
Matrix Spike	100ul Matrix Spike + 100ul of Internal Standard
Recovery Standard	100ul of Recovery Standard + 100ul of Internal Standard

NOTE: With the exception of the recovery standard, all assays are prepared at 1/10 of their normal concentrations and should be evaluated as such.

9.0 SAMPLE PREPARATION

9.1 Aqueous Samples (Continuous Liquid-Liquid Extraction)

9.1.1 Thoroughly rinse the liquid-liquid body and round bottom flask with methylene chloride. Pour 100mL of methylene chloride into the liquid-liquid body. Pour ~~300~~ 175mL of methylene chloride into the round bottom receiving flask and add boiling chips to the round bottom receiving flask.

9.1.2 Remove the samples from the refrigerator and allow the samples to equilibrate to ambient temperature. While the samples are equilibrating to room temperature, prepare the sample labels and begin recording the sample information in the extraction logbook.

9.1.3 Mark the level of the sample on the sample bottle and carefully pour the entire contents into the liquid-liquid body. If there is sediment in the bottom of the container, mix the contents thoroughly and transfer the suspended sediment and water to the liquid-liquid body.

NOTE: If there is a great deal of sediment in the sample, contact the extraction supervisor to determine what should be done with the sample. Large amounts of sediment can clog the tube where the solvent is returned to the receiving flask.

9.1.4 Add approximately 50mL of methylene chloride to the sample container and thoroughly rinse the entire flask with the solvent. Add the solvent to the liquid-liquid body.

9.1.5 Determine the volume of sample in the container by filling the container with water to the mark on the outside of the container. Pour the water into a 1-L graduated cylinder and determine and record the volume of the sample to the nearest 5mL. (This determination can be done at a later time).

9.1.6 Add 1.0mL of the appropriate internal standard solutions to the sample in the liquid-liquid body. The internal standard solutions are added to each sample, blank, lab spike, and matrix spike.

9.1.7 Add 1.0mL of the appropriate matrix spiking solution to all designated laboratory spikes and matrix spike samples (matrix spikes are extracted only if sufficient volume is supplied).

For each batch of twenty or fewer samples, a method blank, a lab control standard (LCS), a matrix spike (MS) and matrix spike duplicate (MSD) (if sufficient sample is supplied) is performed. The method blank for aqueous samples will be performed using a 1.0-L aliquot of reagent water.

If there is not enough sample volume to perform the matrix spikes, the extraction log must be stamped: "Insufficient sample volume was available to perform a batch matrix spike analysis."

9.1.8 Slowly add reagent water to the sample in the liquid-liquid body until the methylene chloride in the liquid-liquid body just spills over into the receiving flask. This will ensure a continuous flow of methylene chloride between the liquid-liquid body and the receiving flask.

9.1.9 Turn on the water condensers and make sure that sufficient water is flowing through the condensers to cool. them. Turn on heat source beneath the round bottom flask and extract for 18 to 24 hours.

9.1.10 After the extraction time has completed, turn the heaters off and allow the receiving flasks to cool. Remove the round bottom flask and pour the contents through a glass column packed with glass wool and approximately 3 cm of baked sodium sulfate into a Zymark tube. The extract is now ready for concentration using the Zymark instrument (SOP EX50).

9.1.11 Transfer the concentrated sample extract to a 40-mL vial followed by several 3-mL hexane rinses. Line the vial cap with aluminum foil and screw on the vial. Sample volume should be approximately 20mL. Store at 4C +/- 2 C until ready for extract clean-up.

9.2 Aqueous Samples (Separatory Funnel)

9.2.1 Remove the samples from the sample refrigerator and allow the samples to equilibrate to ambient temperature. While the samples are equilibrating, prepare the glassware, sample labels, and begin to record the sample information in the extraction logbook.

9.2.2 Thoroughly rinse the 2.0-L separatory funnel with methylene chloride.

9.2.3 Mark the level of the sample on the sample bottle and pour the entire contents into a 2-L separatory funnel. If there is any sediment in the bottom of the container, mix the contents thoroughly and transfer the suspended sediment and water to the separatory funnel.

NOTE: If the sample contains very large amounts of sediment, contact the extraction supervisor to determine a course of action. Large amounts of sediment can clog the stopcock and prevent efficient extraction of the sample.

9.2.4 Add 1.0mL of the appropriate internal standard solutions to the separatory funnel. Mix thoroughly. The internal standard solutions are added to each sample, blank, lab spike, and matrix spike.

9.2.5 Add 1.0mL of the appropriate matrix spiking solutions to all designated laboratory spikes and matrix spike samples(matrix spikes are performed only if sufficient sample is supplied).

For each batch of twenty or fewer samples, a method blank, a lab control standard (LCS), a lab control standard duplicate (LCSD), a matrix spike (MS) and matrix spike duplicate (MSD) (if sufficient sample is supplied) is performed. The method blank for aqueous samples will be performed using a 1.0-L aliquot of reagent

If there is not enough sample volume to perform the matrix spikes, the extraction logbook must be stamped: "Insufficient sample volume was available to perform a batch matrix spike analysis."

9.2.6 Add 100mL of methylene chloride to the sample container and shake for about 20 seconds to thoroughly rinse the container with solvent. Add this methylene chloride rinse to the separatory funnel.

9.2.7 Determine the volume of sample in the container by filling the container with water to the mark on the outside of the container. Pour the water into a 1-L graduated cylinder and determine and record the volume of the sample to the nearest 5mL. (This determination can be done at a later time).

9.2.8 Shake the separatory funnel for 2 min., venting frequently. Vent by removing the stopper of the top opening of the separatory funnel.

CAUTION: Venting the separatory funnel through the stopcock may cause sample extract to be forced out of the funnel into the work area or onto the analyst.

Allow the phases to separate for five minutes and then drain the organic phase (lower layer) into a 600-mL beaker.

9.2.9 Repeat the extraction twice more with fresh 100-mL portions of methylene chloride, combining all extracts into the 600-mL beaker.

9.2.10 Pour the combined extracts through a glass column packed with glass wool and approximately 3cm of sodium sulfate and into a Zymark tube. The extract is now ready for concentration using the Zymark instrument (SOP EX50).

9.2.11 Transfer the concentrated sample extract to a 40-mL vial followed by several 3-mL hexane rinses. Line the vial cap with aluminum foil and screw on the vial. Sample volume should be approximately 20mL. Store at 4C +/- 2 C until ready for extract clean-up.

9.3 Extraction: Soils and Sediments

9.3.1 Remove the samples from the sample refrigerator and allow them to equilibrate to ambient temperature. While the samples are equilibrating to room temperature, prepare the glassware and sample labels and begin recording the sample information in the extraction logbook.

9.3.2 Thoroughly mix the samples and weigh 10.0 to 10.5g of each sample into a 500-mL Erlenmeyer flask.

NOTE: If the sample is difficult to homogenize or of an oily nature, contact the extraction supervisor.

9.3.3 Add 1.0mL of the appropriate internal standard solutions to each sample. Mix thoroughly. The internal standard solutions are added to each sample, blank, lab spike, and matrix spike.

9.3.4 Add 1.0mL of the appropriate matrix spiking solutions to all designated laboratory spikes and matrix spike samples (matrix spikes are performed if sufficient sample is supplied).

For each batch of twenty or fewer samples, a method blank, a lab control standard (LCS), a matrix spike (MS) and matrix spike duplicate (MSD) (if sufficient sample is supplied) is performed The method blank for soils and sediments will be a 10-g aliquot of the same sodium sulfate used to dry the samples. A lab control standard duplicate (LCSD) is prepared and analyzed when there is insufficient sample to perform the MS/MSD.

If there is not enough sample to perform the matrix spikes, the extraction log must be stamped: "Insufficient sample volume was available to perform a batch matrix spike analysis."

9.3.5 Add 10-20g of sodium sulfate to the sample and stir with a glass rod to mix the sample and sodium sulfate. The sample should have a sandy, free-flowing texture.

9.3.6 Add 20mL of methanol to the sample and swirl to mix.

9.3.7 Add 80mL of petroleum ether and swirl to mix.

9.3.8 Stopper the flask and place the samples on the wrist action shaker and extract the samples for two hours.

9.3.9 Pour the extract through a glass column packed with glass wool and approximately 3cm of sodium sulfate and into a Zymark tube. The extract is now ready for concentration using the Zymark instrument (SOP EX50). Evaporate the solvent and adjust to a final volume of 10mL with hexane. Cover the top of the vial with hexane-rinsed aluminum foil and screw the cap on securely. Store at 4C +/- 2C until ready for extract clean-up.

9.4 Acid/Base Clean-up

9.4.1 Transfer the sample extract to a 250-mL separatory funnel. A few milliliters of hexane should be used to complete the quantitative transfer of the extract to the separatory funnel.

9.4.2 Carefully add 50mL of 20% KOH to the funnel, stopper , and shake vigorously for 1 minute. Remove the stopper immediately after shaking (basic solutions can cause glass joints to fuse). Allow the phases to separate. Drain the lower phase in the container for alkali wastes. Washing the extract with the basic solution should be repeated until no color is visible in the lower layer. The base washing of the extract may be repeated a maximum of four times.

NOTE: The extract should not be left in contact with basic solution as this is known to degrade certain PCDD/PCDFs.

9.4.3 Add 50mL of reagent water to the separatory funnel and shake for 1 min. Allow the phases to separate and again drain the lower phase into the alkali waste container.

9.4.4 Carefully add 50mL of concentrated sulfuric acid to the separatory funnel. Heat may be generated when the acid is added to the separatory funnel. Stopper the separatory funnel and shake the separatory funnel for about 1 minute. Use extreme caution when performing the acid wash of the extract. Pressure may increase very rapidly and the funnel may need to be vented frequently.

9.4.5 Remove the stopper and allow the layers to separate. Drain the lower acidic phase into the container for acid wastes. Repeat the acid washing step until <u>no</u> color change is visible in the lower layer. Perform the acid washings a maximum number of four times.

9.4.6 Add 50mL of reagent water to the separatory funnel;. Shake for 1 min. and allow the phases to separate. Drain and discard the lower layer.

9.4.7 Pass the extract through a sodium sulfate drying column and collect the extract in a 40-mL vial. Rinse the drying column with several aliquots of hexane and add the rinses to the extract.

9.4.8 The extract is concentrated down to 2.0mL and split into two 1.0-mL aliquots. If no further cleanup of the extract is required, one of the 1.0-mL aliquots is concentrated to near dryness and then recovered with 100uL of recovery standard (1,2,3,4-TCDD (13C6). The extract is transferred to another 2-mL vial containing a 250uL insert then sealed with septum lined crimp top and stored at 4C +/- 2C until ready for analysis. The remaining aliquot is stored at 4C for further analysis or additional cleanup as needed.

9.5 Alumina Column Cleanup

9.5.1 Pack a glass chromatography column, fitted with a Teflon stopcock in the following manner:

-Insert a glass wool plug into the bottom of the column
-Add a 4g layer of sodium sulfate to the column
-Add a 4-g layer of Woelm super 1 neutral alumina to the column. The alumina need not be activated or cleaned prior to the cleanup but should be stored in sealed desiccator
-Tap the top of the column to gently settle the alumina
-Add a 4-g layer of sodium sulfate to cover the alumina
-Add 10-mL of hexane to the top of the column and open the stopcock. Allow the hexane to drain into a waste container. Close the stopcock when the level of the hexane reached the top of the sodium sulfate layer covering the alumina. The column must not be allowed to go dry from this point.
-Check the column for channeling. Channeling occurs when the alumina and sodium sulfate layers are not properly settled and the solvent eluent flows through channels in the column. If this occurs, discard the column and start again with a new column.

9.5.2 Apply the extract from Section 9.4.8 to the top of the column. Rinse the vial with several small aliquots of hexane to complete the quantitative transfer of the extract to the column.

9.5.3 Open the stopcock on the column and slowly transfer the extract to the top of the alumina. Add enough hexane so the extract is transferred cleanly to the top of the alumina in the cleanup column.

NOTE: The extract must be transferred to the top of the alumina, not just the top sodium sulfate layer.

9.5.4 Elute the column with 10mL of 8% (V/V) methylene chloride in hexane. Capture and retain this portion as a check on the possible breakthrough of the PCDDs and PCDFs if the internal standard recovery is not within the acceptance limits. Again, the column must not be allowed to go dry during this cleanup step.

9.5.5 Elute the column with 15mL of 60% (V/V) methylene chloride in hexane and capture this fraction in a properly labeled concentrator tube.

9.6 Carbon Column Cleanup

9.6.1 Concentrate the 8% (V/V) and 60% (V/V) fractions from the alumina cleanup to 1.0mL. Retain the 8% fraction for possible analysis to determine if breakthrough has occurred in the alumina cleanup.

9.6.2 Prepare the carbon column packing by adding 10g of methanol-cleaned, active carbon and 190g of Type 60: 70 to 230 mesh silica gel into a 600-mL beaker. Activate the mixture at 130C for 6 hours. (This setup should be done well before the samples are ready for the cleanup)

9.6.3 Cut off the ends of a 10-mL glass serological pipet to achieve a 4-inch glass column. Insert a glass wool plug at one end of the column and add 1.0g of the activated carbon/silica gel mixture. Cap the packing with a glass wool plug.

NOTE: Sufficient glass wool should be used to prevent carbon fines from passing into the extract.

9.6.4 Rinse the column with 5mL of cyclohexane/methylene chloride (50:50 V/V) in the forward direction and with 5mL of the same solvent mixture in the reverse direction of the flow. Discard these washings. Perform all of the carbon cleanups at the same time.

9.6.5 While still in the reverse direction of the flow, transfer the sample extract to the column and elute with 10mL of cyclohexane/methylene chloride (50:50 V/V) and 5mL of methylene chloride/methanol(75:25, V/V). Combine and save these eluants.

9.6.6 Turn the column over and elute the column with 25mL of toluene. This fraction should contain the PCDDs and PCDFs.

NOTE: Care should be taken to prevent any carbon fines from slipping past the glass wool plugs. These fines adversely affect the recovery of PCDD/PCDFs.

9.6.7 Concentrate the extract to near dryness and add ~~200~~100uL of the recovery standard to dissolve the residue. The sample extract is now ready for analysis by GC/MS.

10.0 ANALYTICAL PROCEDURES

10.1 Instrument Conditions

10.1.1 Selected Ion Monitoring (SIM) - set to monitor the ions listed in Table 2.

10.1.2 GC Parameters

Injector temperature:	275C
Transfer line temperature:	290C
Source temperature:	factory set at 230C
Injector:	splitless 4 mm ID quartz liner
Sample volume:	2uL
Carrier gas:	helium at 30 cm/s

10.1.3 As needed, the GC is cooled, and the sleeve, septum, syringe, and splitless disc are replaced. Approximately 2 inches of column are removed. The column is reconnected to the injector using a new graphite ferrule. The GC and the various detectors are then reheated to normal operating temperatures.

10.1.4 Temperature Program

Initial column temperature and hold time:	180C for 2.0 minutes (min.).
Column temperature program 1:	70C/min to 235C, hold 1 min., 210-300 @ 5C/min
Column temperature program 2:	8C/min. to 290C (until octa isomers have eluted)

10.2 Tuning

The tune file for the data system is T_NDOX. Ions 264, 414, and 502 are used when tuning for the analysis of dioxins and furans. The object is to maximize 414. It is desired that the peak widths be in the range of 0.58 to 0.60.

10.3 Determination of the RT Windows for the Dioxins and Furans

Injections of furan and window defining mixes are analyzed. From these analyses, the retention time windows for the different isomer groups are established.

10.3 Determination of the RT Windows for the Dioxins and Furans

10.3.1 Perform the column maintenance on the GC and tune the MS to the parameters used for the sample analysis.

10.3.2 Inject the window defining mix . Determine the retention time windows for the different isomer groups.

10.3.3 Update the acquisition method with the correct retention time windows.

10.4 Initial Calibration

10.4.1 After establishing these windows, analyze each calibration standard. Two microliters (2uL) of the calibration standards are analyzed. The 25ng/mL is not used for the hepta or octa dioxin/furan calibration curves.

Calculate the response factors for each compound as follows:

$$Rf_x = \frac{(Ax)(Cis)}{(Ais)(Cx)}$$

where

Ax = area of characteristic ion for the compound being measured
Ais = area of the characteristic ion for internal standard
Cx = theoretical concentration of the compound being measured (ng/mL)
Cis = theoretical concentration of the internal standard (ng/mL)
Rf_x = response factor for the compound being measured

10.4.3 The average RF and percent relative standard deviation are calculated for each compound. The %RSD for each compound must be less than 15% for method 8280 and less than 10% for method 613. If the criteria is not met for method 8280, corrective action must be taken and the system recalibrated. If the <10% RSD criteria is not met for method 613, a calibration curve of response ratios may be used. Although no method criteria for a curve is specified, STL Savannah's criteria will be a correlation coefficient of >= 0.990 for the curve.

$$\%RSD = \frac{standard\ deviation}{Avg.RF} \otimes 100$$

10.4.4 The average m/z ratio for each isomer group being calibrated must meet the criteria listed in Table 1.

10.5 Continuing Calibration

10.5.1 Prior to the analyses of samples, a continuing calibration verification (CCV) standard must be analyzed. The 12-h/24-h clock begins when the CCV is injected. The 100 ng/mL standard is used as the CCV.

10.5.2 The response factor and the percent difference for each compound should be calculated and compared with the average RF from the latest five-point calibration. The percent difference for each compound must not exceed 30% for method 8280 or 15% for method 613. If a curve was utilized for method 613, the calculated value must not exceed 15% relative to the theoretical value. The m/z ratios for each compound must meet criteria listed for the initial calibration.

The following criteria must be met using m/z 334:

Check the resolution between 1,2,3,4-TCDD-13C12 and 2,3,7,8-TCDD-13C12. The percent valley of the peaks must not exceed 25% from baseline to valley relative to peak height of the smaller peak.

The following criteria must be met using m/z 320:

The signal-to-noise ratio must be greater than 50:1 a 2,3,7,8-TCDD.

10.6 Analytical Sequence

10.6.1 The extract is contained in an autosampler vial at a final volume of 0.2mL. The GC/MS conditions are listed in Section 10.1. Samples are analyzed using selected ion monitoring (SIM) for the ions found in Table 2.

When sample extracts are found to contain positive hits above the calibration range or when the matrix interferes with the analysis, the sample must be diluted. Internal standards should not be used to quant if diluted beyond 10% of its response in the calibration verification standard. If an extract dilution is necessary, then quantitation of targets must be done using the recovery standard. Use the same equations for evaluation of the initial and continuing calibrations, substituting the response and concentration of the recovery standard for the internal standard(s). The concentrations of the target analytes are calculated using the equations in Section 11.2, again substituting the response and concentration of the recovery standard in place of the internal standard. Not that in this case, the recovery standard will be used to calculate the concentration of all target parameters.

NOTE: If the recovery standard is used for quantitation because of dilution of the internal standards, the initial and continuing calibrations associated with the sample(s) must be reevaluated using the response and concentration of the recovery standard and all initial (%RSD) and all continuing calibration (%difference) criteria must be met.

ANALYTICAL SEQUENCE

I) Window-defining mixes (analyzed when new columns installed or column maintenance perfromed)
-Dioxins/Furans

II) Initial Calibration Standards
-5 calibration standards
-evaluation of the resolution between 1,2,3,4-TCDD-13C12 and 2,3,7,8-TCDD-13C12
-evaluation of signal-to-noise ratio

III) Sample analyses until: 12-hour clock expires - Method 8280
24-hour clock expires - Method 613

IV) Continuing Calibration Standard
-100ng/ml calibration standard
-evaluation of the resolution between 1,2,3,4-TCDD-13C12 and 2,3,7,8-TCDD-13C12
-evaluation of signal-to-noise ratio

VI) Sample analyses until: 12-hour clock expires - Method 8280
24-hour clock expires - Method 613

This sequence ends when one of the continuing calibration criteria cannot be met. When one of the criteria is not met, the sequence must be started again to include the initial calibration.

10.6.2 Identification Criteria for PCDDs and PCDFs

To positively identify an isomer, the following criteria must be met:

10.6.2.1 Both the primary and confirmation ions (characteristic ions) must be present (see Table 2). Additionally, it is desired that the M-COCL ion should also be present.

10.6.2.2 Maximum intensity of characteristic ions must coincide within 2 scans or 2 seconds.

10.6.2.3 Once the retention time criteria is met, a check will be performed to assure proper integration (valley to valley) of all ion profiles. In the event the data system improperly integrates an ion profile peak, manual integration of the peak(s) using the data system software will be performed. The before and after integration should be retained and initialed/dated by the analyst performing the manual integration.

10.6.2.4 Relative intensity of isotopic ions must lie within range specified in Table 1 for method 8280. The ratio of m/z 320 and mz/ 322 must agree within 10% of the response ratio demonstrated in the continuing calibration standard for method 613.

10.6.2.5 The isomer must reside within the retention time window previously established for the homologous series of that particular isomer.

10.6.3 Identification Criteria for 2,3,7,8-TCDD

Method 8280 does not address RT window criteria for positive identification of 2,3,7,8-TCDD; therefore, STL Savannah defaults to CLP SOW DFLM01.1, page D-42, Section 11.1 which states:

In order to make a positive identification of the 2,3,7,8-substituted isomers for which an isotopically labeled internal or recovery standard is present in the sample extract, the absolute retention time at the maximum peak height of the analyte must be within -1 to 3 seconds of the retention time of the corresponding labeled standard.

The peak tentatively identified as 2,3,7,8-TCDD must also meet the criteria for identification as a tetra chlorinated dibenzo dioxin.

Method 613 specifies that the retention time of the masses 320, 322, and 257 for 2,3,7,8-TCDD must match that of the calibration standard within the performance specifications of the analytical system. This guidance would be the equivalent of that dictated above for the CLP SOW.

11.0 CALCULATIONS

11.1 Internal Standards

The two internal standards are taken through the entire extraction process. At the end of the extraction, a recovery standard is added. Although method 613 addresses an internal standard concentration of 25ng/ml, it is not appropriate for this low resolution GC/MS SIM procedure; therefore, SW-846 method 8280 guidance for internal standard concentrations is utilized. All three standards are added at a concentration of 500ng/mL and the percent recovery of the internal standards can be calculated as follows:

$$\%REC = \frac{Ais}{Arec} \otimes \frac{1}{RFavg} \otimes 100$$

where

Ais = area internal standard
Arec = area of the recovery standard
Rfavg = average response factor from five-point of internal standard relative to the recovery standard.

The % recovery criteria of the two internal standards must be > 40% for method 8280; however, any recovery < 40% or > 120% would indicate the need for reextraction and/or reanalysis. Method 613 internal standard criteria specifies that the area of the internal standard must be >50% of the area for the internal standard in the continuing calibration standard or corrective action including reextraction and/or reanalysis must be taken.

The OCDD ($^{13}C_{12}$) internal standard is only required when the analysis of the hepta or octa dioxin/furan isomers are needed.

11.2 Target Compounds

When a compound has been identified, the quantification of that compound is based on the abundance of the characteristic ion. Quantitation takes place using the internal standard technique.

Internal Standards with Corresponding Isomers Assigned for Quantitation

$^{13}C_{12}$ 2,3,7,8-TCDD
-Tetra Dioxin/Furan isomers
-Penta Dioxin/Furan isomers
-Hexa Dioxin/Furan isomers

$^{13}C_{12}$ Octa-TCDD
Hepta Dioxin/Furan isomers
-Octa Dioxin/Furan isomers

NOTE: If the recovery standard must be used for quantitation, all target parameters (tetra through octa dioxins and furans) will be quantified using the recovery standard.

Calculate the concentration of each identified compound as given below.

Aqueous Matrix

$$Concentration\,(ug\,/\,L) = \frac{(Ax)\,(Is)\,(Vt)}{(Ais)\,(RFavg)\,(Vo)\,(Vi)} \otimes \frac{1\,ug}{1000\,ng}$$

Ax =	Area of the characteristic ion of the compound
Is =	Weight of internal standard injected (ng)
Vt =	Extract volume (uL)
Ais =	Area of characteristic ion of the appropriate internal standard
Vi =	Volume injected (uL)
RF avg =	Average response factor for the compound relative to the internal standard
Vo =	Sample volume extracted (L)

Sediment/Soil(Dry Weight Basis)

$$Concentration\,(ug/kg,dw) = \frac{(Ax)(Is)(Vt)}{(Ais)(RFavg)(Ws)(D)(Vi)} \otimes \frac{1\,ug}{1000\,ng}$$

Ws = Sample weight of sample extracted (kg)
D = (100% - % moisture in sample)/100%, or 1 for a wet weight basis
Ax = Area of the characteristic ion of the compound
Is = Weight of internal standard injected (ng)
Vt = Extract volume (uL)
Ais = Area of characteristic ion of the appropriate internal standard
Vi = Volume injected (uL)

12.0 QUALITY CONTROL/QUALITY ASSURANCE

SOP AN02:*Analytical Batching* contains the equations for the calculation of the percent recovery and relative percent difference of the QC items. This SOP also contains guidance for the evaluation of QC, including guidance for corrective actions.

12.1 Required Instrument QC (Calibration)

Each 12-h period (method 8280) or 24-h period (method 613), the daily calibration standard must be evaluated to determine if the five point calibration is still valid and if the chromatographic system is operating properly. If the continuing calibration criteria is not met, the initial calibration must be performed.

Check to see if criteria for % valley and signal-to-noise are met.

Check to see if the peaks and responses look normal. If any changes are made to the chromatographic system, recalibration must take place.

The laboratory must maintain records to document the quality of the data generated. All raw data and quality control documentation must be kept for a minimum of five years.

12.2 Method Blank

12.2.1 With each batch of 20 analytical samples or with each matrix change, a reagent water method blank or sodium sulfate method blank must be carried through all stages of the sample preparation and measurement. The method blank is used to monitor and ensure that interferences from the analytical system, glassware, and reagents are under control.

12.2.2 The method blank must contain less than or equal to the reporting limit (RL) for all target compounds. Also, the internal standard percent recoveries must be within 40 to 120% for method 8280 and 50% of the IS area in the continuing calibration standard for method 613.

12.2.3 If a method blank exceeds the RL for any target compound, or if any one internal standard is out of control, a nonconformance/corrective action report will be filled out and the following corrective action will be taken:

1. Sources of contamination will be investigated. Possible sources include the analytical system, glassware, syringes, or extraction contamination.

2. If the analytical system is in question, the method blank will be reanalyzed on another instrument. If all contamination disappears, the samples associated with the blank will be analyzed on the uncontaminated system. If the contamination is still present, the samples will be re-extracted and reanalyzed.

With each set of 20 samples, or for a particular matrix, two matrix spikes, (if requested by client), and a laboratory spike (reagent water or sodium sulfate spikes) must be carried through all stages of the sample preparation and measurement. Method 613 requires laboratory spikes at a frequency of 10% if the matrix spikes do not meet criteria. The spikes contain one congener from each homologous series of 2,3,7,8 dioxin and furan isomers.

12.3 Spikes/Internal Standards

Compare the %Rec and RPD values with the acceptance criteria in the Laboratory Quality Manual. If any of the matrix spike %Rec values are outside the limits, evaluate the lab spike. If the lab spike %Rec value is outside the limits, then the entire group of extracts is questionable and the samples and associated QC must be re-extracted and reanalyzed. If however, the lab spike falls within the acceptance criteria, then the sample data is considered valid and the nonconformance of the matrix spikes is deemed to be due to matrix interference. It may be necessary to reanalyze spikes if the problem appears to be instrumental in nature.

The internal standard recovery for each sample analyzed must be within 25 to 150% for method 8280 or >50% IS area relative to the continuing calibration standard for method 613. If the recoveries of the internal standards fall outside of these limits, it is recommended that the sample be reanalyzed. If the recoveries of the internal standards fall within the criteria upon reanalysis, the reanalysis results are reported. If the reanalysis is still outside of criteria, the sample is re-extracted and reanalyzed. If after re-extraction, the sample still does not meet the criteria, then data must be flagged and a nonconformance report must be written explaining the problem is due to matrix effect.

12.4 Method Detection Limits

The method detection limit (MDL) must be performed annually in accordance with SOP CA90: *Procedure for the Determination of the Method Detection limit (MDL)*.

12.5 Each analyst who performs this procedure must complete an initial demonstration of capability (IDOC) in accordance with SOP CA92: *Evaluation of IDOCs*.

13.0 PREVENTIVE MAINTENANCE AND TROUBELSHOOTING

PREVENTIVE MAINTENANCE SCHEDULE								
EQUIPMENT ITEM	**Service Interval**							**SERVICE LEVEL**
	D	W	M	Q	SA	A	AN	
GAS CHROMATOGRAPH - MASS SPEC SEMIVOLATILES								
Column/Injector							X	Change sleeve and cut front of column.
Septum	X							Replace as needed.
Gas Cylinder	X							Inspect daily, change when pressure reads <500 psi.
Hydrocarbon/Moisture Trap							X	Replace.
Splitless Disc							X	Replace.
Autosampler							X	Syringe and tubing cleaned. Needles and tubing replaced.
Rough Pump							X	Oil changed by HP service.
Mass Spectrometer							X	Clean.
Tape Head							X	Clean.
Tape Drive							X	Clean.

D =daily; W = weekly; M = monthly; Q = quarterly; SA = semi-annually; A = annually; AN = as needed

14.0 WASTE MANAGEMENT AND POLLUTION PREVENTION

All samples, sample extracts, and excess standards and reagents must be disposed in accordance with SOP CA70: *Waste Management*.

15.0 REFERENCES

1. Test Methods for Evaluating Solid Waste, Third Edition; U.S. EPA Office of Solid Waste and Emergency Response: Washington, DC,. Method 8280

2. Code of Federal Regulations, Title 40, Part 136; US Government Printing Office: Washington, DC.

TABLE 1-Tuning Masses and Acceptable Ratios			
	Ratio	M/Z	
		Furans	Dioxins
Tetra	0.65 - 0.89	304/306	320/322
Penta	0.55 - 0.75	342/340	358/356
Hexa	0.69 - 0.93	376/374	392/390
Hepta	0.83 - 1.12	410/408	426/424
Octa	0.75 - 1.01	442/444	458/460

TABLE 2
IONS SPECIFIED FOR SELECTED ION MONITORING FOR PCDDs AND PCDFs

	Quantitation Ion	Confirmation Ion	M-COC1
PCDDs			
$^{13}C_{12}$ Tetra (ISTD)	334	332	—
Tetra	322	320	257
Penta	356	354; 358	293
Hexa	390	388; 392	327
Hepta	424	422; 426	361
Octa	460	458	395
$^{13}C_{12}$ Octa (ISTD)	472	470	—
PCDFs			
Tetra	306	304	243
Penta	340	338; 342	277
Hexa	374	372; 376	311
Hepta	408	406; 410	345
Octa	444	442	379

ISTD = Internal Standard

TABLE 3

SPIKE (SPK) AND INTERNAL STANDARD (ISTD) RECOVERY AND RPD LIMITS

	Water	Soil
	% Rec	**% Rec**
$^{13}C_{12}$-2,3,7,8-TCDD (ISTD) (Method 8280)	25-150	25-150
$^{13}C_{12}$-2,3,7,8-TCDD (ISTD) (Method 613)	>50*	NA
$^{13}C_{12}$-OCDD (ISTD) (Method 8280)	25-150	25-150

*area of the $^{13}C_{12}$-2,3,7,8-TCDD in the sample relative to the area in the continuing calibration standard.

FREE PRODUCT (NAPL) MOBILITY - CENTRIFUGAL METHOD PROCEDURE

(Method: ASTM D425M-88)

Purpose
The purpose of this test is to demonstrate whether NAPL present in a soil is mobile and if so, what is the residual saturation after mobile NAPL is removed from the soil. ASTM Method D425 is used to provide a starting point for the methodology and is chosen because it is relatively simple, has widespread usage, and 1000 X Gravity when applied for one hour is a conservative value for driving a sample to a residual saturation.

Method Summary
Free product (NAPL) mobility of soils is determined by inserting undisturbed (native-state) samples into Beckman type PIR 16.5 rotor and standard rock (soil) core buckets (centrifuge cups) and centrifuging for 1 hour at a force equal to 1000 times that of gravity at a controlled temperature of 20 ± 1°C. Fluids produced during centrifuging and collected and volumes measured. Residual fluid saturations are determined by Dean-Stark extraction and sample properties determined at completion of the centrifuge run.

Sample Preparation
The core is maintained in frozen condition to preserve water and NAPL saturations.

A one and one-half inch (1-1/2") diameter sample is cut from core selected by CLIENT COMPANY personnel for free product mobility; residual, and initial saturation analyses. The sample is cut parallel to core axis (vertical) and tested in native-state condition.

A flexible Teflon jacket and stainless steel end screens are applied to the sample.

Free Product (NAPL) Mobility
Following cutting and packaging, the sample is allowed to thaw and is then loaded into a centrifuge cup for free product mobility evaluation. A centrifugal force of 1000 times gravity is applied to the sample for one hour (ASTM D425M). The sample is monitored for mobile NAPL (produced NAPL) and water production.

a. Record volume of any NAPL produced.
b. Record volume of any water produced.
c. Record all visual observations of sample behavior and produced fluids.

Sample Properties
Following spinning at 1000 X G for one hour, the sample is removed from the centrifuge cup and extracted with toluene (Dean-Stark method) for residual saturations (fluid saturation confirmation). Initial saturations are determined by material balance (fluid summation). Following Dean-Stark extraction, the sample is dried to stable weight and sample properties (porosity, dry bulk density, and grain density) determined.

Reporting
Data is reported in tabular format and can be presented in an EDD format.

FREE PRODUCT (NAPL) MOBILITY - CENTRIFUGAL METHOD PROCEDURE

(Method: ASTM D425M-88)

Modifications to ASTM D425

1.1 Covers determination of residual saturation and NAPL mobility by centrifuge method.
1.2 This test uses *undisturbed* specimens of rock or soil.
4.1 Residual saturation determination is conducted on a native-state (undisturbed) sample by centrifuging for 1 h at a force equal to 1000 times that of gravity at a controlled temperature of 20 ± 1°C. Fluids produced are monitored for mobility evaluation and material balance calculations.
5.2 When water and NAPL are present in a sample, the centrifuge moisture equivalent approximates conservative residual saturations for water and NAPL.
6.1-6.3 Beckman type PIR 16.5 rotor and standard rock (soil) core buckets (centrifuge cups) are used for centrifuging samples.
6.6-6.10 The samples are tested in undisturbed condition and Dean-Stark extraction method (API RP40) is used to determine residual saturations.
7.1-7.2 The samples are tested in undisturbed condition. A 1-1/2"dia. x 2" long sample is used.
8.1 A native-state (undisturbed) sample is placed in the centrifuge cup for centrifuging.
8.4 Immediately after centrifuging, the volume or mass of fluids produced is recorded and the sample is weighed and placed in the Dean-Stark extraction vessel. Following Dean-Stark extraction, bulk density and porosity are determined.
9.1 The test may be performed on only one sample due to core or material availability constraints.
10.1.2 Post-centrifuging residual saturations and pre-centrifuging initial saturations are reported as pore fluid saturations, percent pore volume.

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SAMPLE PREPARATION FOR PARTICLE SIZE ANALYSIS PROCEDURE
(ASTM D421/422M Method)

Sampling

1. Sub-sample approximately 20-30 grams of representative material at the requested interval.
2. Break up aggregations using a wood or rubber-covered pestle.
3. Dry sample at room temperature until weight is stable.
   a. If RUSH turnaround time is required, dry sample at 150°F until weight is stable.
   b. If sample is contaminated with petroleum hydrocarbons, sample must be cleaned.
      i. Package sample in thimble or cellulose envelope for Dean-Stark or Soxhlet extraction.
      ii. Extract for 4-8 hours or until sample is clean.
      iii. Dry sample at 150°F in vacuum oven until weight is stable.
4. For LPSA analysis, material passing a No. 10 (2.00-mm) sieve is required.
5. **Note:** For non-sediment (soil) samples, contact client to develop procedure.

LPSA Sample Preparation

1. Disaggregate sample material to grain size using wood or rubber-covered pestle being careful not to break individual grains.
2. Separate test sample by sieving with a No. 10 (2-mm) sieve.
   a. Record weight of any retained material and passing material weight.
3. By use of a micro sample splitter, select a portion of sample suitable for occlusion (8-12 percent occlusion) of the Laser Particle Size Analyzer (LPSA).
4. Place the sample in a 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution.
   a. A solution of sodium hexametaphosphate is prepared at a rate of 40 grams of sodium hexametaphosphate per liter of distilled or demineralized water.
   b. Stir or agitate until the soil is thoroughly wetted.
   c. Allow to soak for at least 16 hours.
5. Following soaking period, disperse sample prior to introduction into Laser Particle Size Analyzer.
6. Stir with stainless steel or glass stirrer or use sonicator.
7. **Note:** For non-sediment (soil) samples, contact client to develop procedure.

LPSA Analysis

1. Wash sample into LPSA fluid module using distilled or demineralized water making sure all sample is washed from beaker.
2. Allow to circulate for at least 20 seconds or until the sample is completely dispersed before measuring.
3. Measure sample particle size distribution per Method ASTM D4464M.

Test results are presented in tabular and graphical formats.

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PORE FLUID SATURATIONS - DISTILLATION EXTRACTION PROCEDURE

(Method: Dean Stark, API RP 40)

Scope

Pore fluid saturations of plug samples drilled, cut, or formed from whole cores are determined using a solvent boiling flask, thimble, calibrated sidearm, and condenser. The samples may contain naturally occurring hydrocarbons, be contaminated with refined hydrocarbons (LNAPL's or DNAPL's) from leaks or spills, or hydrocarbons from other processes. The method uses solvent distillation to remove pore fluids (hydrocarbons and water) from the plug samples and material balance (gravimetric and volumetric methods) to summarize the fluids. Sample basic properties (pore volume, bulk volume) must be determined separately in order to report the fluid saturations as percent pore space or bulk volume.

Method Summary

Refer to API RP 40 Section 4.3 and Yeung et al, 1994 for method description.

Quality Control

Refer to API RP 40 Section 4.3 and Yeung et al, 1994 for limitations and accuracy/precision.

Reporting

Data is reported in tabular format and can be presented in an EDD format.

Laboratory Procedure

1. Weigh native sample to 0.01gm.
2. Place sample in dried cellulose extraction thimble.
3. Place thimble in distillation flask.
4. Fill boiling flask 2/3 full with toluene.
5. Assemble system.
6. Turn on heater and monitor water distilled into the water trap.
7. When water production stabilizes continue extraction for 1 hr.
8. Turn off heater and allow system to cool to room temperature.
9. Read extracted water volume to 0.01ml.
10. Remove thimble from distillation flask.
11. Dry to a stable weight at 150°F in a vacuum oven.
12. Record sample weight at ambient temperature to 0.01gm.
13. Calculate water weight:

    Wt. water = (volume of water x density of water)

14. Calculate hydrocarbon weight:

    Wt. Hydrocarbon = ((sample initial weight - sample dry weight) - water weight)

Blank Acceptance Range: 0.01gm
Standard Acceptance Range: 80-120%

Optional: Convert extracted weights to volumes and express as percentage of pore space saturation. Requires Porosity measurement.

PORE FLUID SATURATIONS - DRYING PROCEDURE

(Method: Dean Stark, API RP 40)

This document covers the standard procedure for extraction and drying of samples for pore fluid saturation determination. ANY deviation must be pre-approved by your Supervisor or Manager BEFORE proceeding. Job or Site specific instructions will take precedent.

1. Obtain samples from specified locations in requested orientation (horizontal or vertical).
2. Package for appropriate test program.
3. Record "WET SAMPLE PACKAGE WEIGHT" on data sheet with date and technician initials.
4. Place sample in dry extraction thimble with tissue on top and bottom of plug.
5. Record "WET SAMPLE + THIMBLE WEIGHT" on data sheet with date and technician initials.
6. Place thimble containing sample in prepared extraction unit with dry tube on condenser.
7. Record "SIDEARM NUMBER" on data sheet with date and technician initials.
8. Extract sample until water production stops.
   a. If water production exceeds sidearm volume, cool extractor, remove and record excess water on data sheet.
   b. Continue extraction until water production stops.
   c. Repeat 8a – 8b until final water reading can be taken without exceeding sidearm volume.
9. Cool extraction unit to room temperature.
10. Remove trapped toluene from sidearm water by adding 2-3 grains of dry soap and "twiddling" using appropriate brass rod.
11. Record final water volume and room temperature on data sheet.
12. Have 2nd technician verify water volume reading and initial data sheet BEFORE sample is removed from extractor.
13. Remove water from sidearm.
14. Remove thimble with sample from extraction unit being careful not to damage thimble.
15. Place thimble with sample in ventilating unit to remove excess toluene for 2-hours.
16. Place thimble with sample in vacuum oven and dry to stable weight.
17. Record weights on "Core Analyses Dry Weight Monitor" sheet with date and technician initials.
    a. Stable weight is +/- 0.01 gm over 4-hour period.
18. Place thimble and sample in "Plug Sample Only" drying oven at 150°F and dry to stable weight.
    a. Stable weight is +/- 0.01 gm over 4-hour period.
19. Record weights on "Core Analyses Dry Weight Monitor" sheet with date and technician initials.
20. Record final "THIMBLE + SAMPLE DRY WEIGHT" on data sheet(s) with date and technician initials.
21. Remove sample from thimble and record final "SAMPLE DRY WEIGHT" on data sheet(s) with date and technician initials.
    a. Note any grain loss in thimble and notify your supervisor BEFORE proceeding to next analysis step.

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PORE FLUID SATURATIONS - DISTILLATION EXTRACTION FLOW CHART

(Method: Dean Stark, API RP 40)

FREEZE CORE → PREPARE EXTRACTORS

PREPARE EXTRACTORS
↓
DRY DESSICATOR TUBE AT 105°C
↓
ADD 4-5 ML OF WATER TO FLASK*
↓
BOIL TOLUENE IN EXTRACTION FLASK ½-1 HOURS
↓
SUCK SIDEARM DRY (VACUUM)
↓
BOIL TOLUENE IN EXTRACTION FLASK FOR ½-1 HOURS
↓
SUCK SIDEARM DRY (VACUUM)
↓
ATTACH DRY DESSICATOR TUBE
↓
PLACE SAMPLE IN EXTRACTION FLASK → BEGIN EXTRACTION RUN

FREEZE CORE
↓
CUT SAMPLE
↓
PACKAGE SAMPLE
↓
WIPE OUTSIDE OF SAMPLE WITH FOR TISSUE OR PAPER TOWEL
↓
WEIGH SAMPLE & RECORD WET WEIGHT
↓
KEEP SAMPLE BATCH FROZEN
↓
WIPE OUTSIDE OF SAMPLE WITH TISSUE OR PAPER TOWEL
↓
PLACE SAMPLE IN DRY THIMBLE
↓
WEIGH THIMBLE + SAMPLE AND RECORD WET WEIGHT
↓
PLACE SAMPLE IN EXTRACTION FLASK
↓
BEGIN EXTRACTION RUN
↓
EXTRACT FOR MINIMUM 8-12 HOURS
↓
TAKE WATER READINGS AT ROOM TEMPERATURE
↓
IF WATER VOLUME IS > SIDEARM, RECORD MULTIPLE READINGS AND EXTRACT FOR AN ADDITIONAL 1-2 HOURS
↓
COOL TO ROOM TEMPERATURE AND TAKE FINAL WATER READING
↓
REMOVE SAMPLE FROM EXTRACTION FLASK
↓
PLACE SAMPLE IN AIR FOR PRELIMINARY DRYING
↓
VACUUM DRY*
↓
OVEN DRY AT 150°F
↓
MONITOR SAMPLE DRY WEIGHT UNTIL STABLE

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VISCOSITY OF NAPL PROCEDURE

(Method: ASTM D445)

Scope

This procedure covers the determination of the kinematic viscosity of both transparent and opaque fluids. The fluids may be either water or liquid hydrocarbons (crude or refined petroleum products). The method consists of measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity is obtained by multiplying the kinematic viscosity by the liquid density.

Method Summary

Refer to ASTM D445 for method description.

Quality Control

Refer to ASTM D445 for limitations and accuracy/precision.

Reporting

Data is reported in tabular format and can be presented in an EDD format.

Laboratory Procedure

1. Bring NAPL sample to room temperature.
2. If viscosity data is to be used for permeability measurements, filter appropriately.
3. Adjust viscosity baths to test temperatures.
4. Fill out viscosity test sheet with sample ID, your initials, test date, test temperature(s), viscometer number and constant. Record sample density if available.
5. Pour ~100 mls of NAPL into a clean beaker.
6. Select appropriate viscometer for type of oil. The time for the test at each temperature should be as close to 200 seconds as possible.
7. Using a disposable dropper, fill the crossarm viscometer up to the line. Note that after heating, some oil may need to be withdrawn
8. When testing at multiple temperatures, fill additional viscometers as needed.
9. Place viscometer into the bath making sure that both lines are under the bath surface and allow 20 minutes for the viscometer to come to temperature.
10. Using an aspirator, push or pull oil until it siphons through the capillary. When the oil reaches the first line start the stopwatch. When the oil reaches the second line stop the stopwatch and record the time.
11. When the NAPL level reaches the top line start the stopwatch.
12. When the NAPL level reaches the bottom line, stop the stopwatch and record time.
13. Repeat steps 10-12 two additional times. Readings should not vary more than 5%. If they do, inspect viscometer for particulates in the fine capillary sections.
14. Repeat steps 10-13 for additional test temperatures.
15. Using a vacuum, draw toluene through the viscometer until clean. Follow with a small amount of acetone, and then dry.

Optional: Measure the density of fluid to convert kinematic viscosity to dynamic viscosity;

Dynamic Viscosity, Centipoise = Kinematic Viscosity, Centistokes x fluid density, g/cc

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VISCOSITY OF WATER PROCEDURE

(Method: ASTM D445)

Scope

This procedure covers the determination of the kinematic viscosity of both transparent and opaque fluids. The fluids may be either water or liquid hydrocarbons (crude or refined petroleum products). The method consists of measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer. The dynamic viscosity is obtained by multiplying the kinematic viscosity by the liquid density.

Method Summary

Refer to ASTM D445 for method description.

Quality Control

Refer to ASTM D445 for limitations and accuracy/precision.

Reporting

Data is reported in tabular format and can be presented in an EDD format.

Laboratory Procedure

1. Bring water sample to room temperature.
2. If viscosity data is to be used for permeability measurements, filter appropriately.
3. Adjust viscosity baths to test temperatures.
4. Fill out viscosity test sheet with sample ID, your initials, test date, test temperature(s), viscometer number and constant. Record sample density if available.
5. Pour ~100 mls of water into a clean beaker.
6. Invert Cannon-Fenske viscometer and submerge the smaller diameter section in the water. Most waters will be tested using a number 50 viscometer.
7. Using an aspirator, draw water up the capillary until it is even with the second line. Always position your eye so that when viewing the line you see only one (no parallax).
8. Invert viscometer. It is now ready for use.
9. When testing at multiple temperatures, fill additional viscometers as needed.
10. Place viscometer into the bath making sure that both lines are under the bath surface and allow 20 minutes for the viscometer to come to temperature.
11. Using the aspirator, draw water up the capillary past the top line.
12. When the water level reaches the top line start the stopwatch.
13. When the water level reaches the bottom line, stop the stopwatch and record time.
14. Repeat steps 10-12 two additional times. Readings should not vary more than 5%. If they do, inspect viscometer for particulates in the fine capillary sections.
15. Repeat steps 10-13 for additional test temperatures.
16. Using a vacuum, draw DI water through the viscometer until clean. Follow with a small amount of acetone, and then dry.

Optional: Measure the density of fluid to convert kinematic viscosity to dynamic viscosity;

Dynamic Viscosity, Centipoise = Kinematic Viscosity, Centistokes x fluid density, g/cc

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DETERMINATION OF APPARENT SURFACE AND INTERFACIAL TENSION

(Method: ASTM D971)

Scope
This procedure covers the measurement of the interfacial tension of Non-Aqueous Phase Liquids (NAPL's) against water. The procedure is modified to include the measurement of apparent surface tension of NAPL against air and water against air.

Method Summary
Refer to ASTM D971 for method description.

Quality Control
Refer to ASTM D971 for limitations and accuracy/precision.

Reporting
Data is reported in tabular format and can be presented in an EDD format.

Laboratory Procedure

Cat. Nos. 70535 and 70545 Tensiometers are supplied completely assembled and in a metal case. No. 70537 6-cm Platinum-Iridium Ring is supplied with No. 70535 Tensiometer. No. 70542 6-cm Platinum-Iridium Ring is supplied with No. 70545 Tensiometer.

In these instructions the following points will be discussed: (1) preparing the instrument for use, (2) procedure and determination of apparent surface and interfacial tension, and (3) applying correction factor to obtain true value of surface and interfacial tension.

In addition to these instructions the user is referred to the publications listed on page 8 of these instructions.

1. PREPARING THE INSTRUMENT FOR USE

These tensiometers are used in the measurement of small forces. They are of necessity delicate Instruments and should be handled carefully and thoughtfully. Keep the Instrument clean and in good operating condition. When not in use keep it in the case.

The platinum ring must be handled carefully. To obtain accurate results the ring must be clean and in good condition. The ring must be in one plane and round. See page 4 for suggestions on cleaning the ring.

Both instruments are calibrated so that the dial reading is the apparent surface tension expressed in dynes per centimeter. If a known weight M is placed on the ring and balanced by the torsion in the wire, then the dial reading p is given by the equation

$$P = \frac{Mg}{2L}$$

where

M = weight expressed in grams
g = value of gravity in cm/sec^2
L = mean circumference of ring in centimeters
p = dial reading = apparent surface tension in dynes per cm

DETERMINATION OF APPARENT SURFACE AND INTERFACIAL TENSION

(Method: ASTM D971)

Cat. No. 70545 Tensiometer
Carefully remove the tensiometer from the case. Remove the paper wedge supporting the upper bearing. Remove the instrument from the wooden base and place on a level and stable bench free from vibration. Level the Instrument by means of leveling screws until a small level placed on the sample table indicates the table is horizontal.

The instrument is shipped with the torsion wire taut, with the counterweight (E), Pig. 4, properly set, and in approximate adjustment as regards calibration. Further adjustment now consists of an exact calibration so that the dial will indicate directly in dynes per centimeter. This exact calibration is accomplished by adjusting the lengths of the torsion arms (M). The cover over the torsion wire must be removed. The lengths of these arms may be changed by means of the nuts (Q), one on the upper arm and one directly below on the lower arm. Always turn these nuts the same amount so as to maintain equality of length of the torsion arms.

With the vertical arm (P) locked by the clamping screw (N), Fig. 3, insert the shaft of the platinum ring into the lower end of this arm. When (N) is released see that the vertical arm moves freely up and down between the clamping jaws (X). Fit a small strip of paper on the ring to serve as a platform. Open the adjustable stops (D) and with knurled knob (A) bring the index (I) and its mirror image exactly in line with the reference line on the mirror. Loosen the dial clamp (C) and rotate the dial until the vernier indicates zero. Tighten the clamp and use the fine adjustment screw (F) to bring the zero of the dial exactly opposite the zero of the vernier. The tensiometer is now ready for the actual calibration which consists of adjusting the torsion arms to make the dial of the Instrument read directly in dynes per centimeter.

Place on the paper platform on the ring some accurately known weight of between 500 and 800 milligrams. Turn the knurled knob (A) until the Index (I) is exactly opposite the reference line on the mirror. Record the scale reading to 0.10 divisions.

Assuming that a weight of 800 milligrams is used, substitute in Equation (1) and determine what the dial reading and hence the surface tension should be. As an example,

M = 0.800 gram
L = 6.00 cm (use value given on box)
g = 980.3 cm/sec^2 (at Chicago)

then

$$p = \frac{Mg}{2L} = \frac{0.8 \times 980.3}{2 \times 6.00} = 65.35 \text{ dynes/cm}$$

If the recorded dial reading is greater than the calculated value adjust the nuts (G) to shorten the torsion arms. If the dial reading is less adjust the nuts to lengthen the arms. Take care to always lengthen or shorten the arms exactly the same amount so as to maintain the vertical arm of the moving system exactly vertical. Repeat the calibration procedure, removing the weight and readjusting the zero setting with paper in place after each change in length of the arms, until the dial reading agrees with the calculated value. Each unit on the dial then represents a tension of exactly one dyne per centimeter in either direction from zero.

DETERMINATION OF APPARENT SURFACE AND INTERFACIAL TENSION

(Method: ASTM D971)

2. PROCEDURE AND DETERMINATION OF APPARENT SURFACE AND INTERFACIAL TENSION

In making surface and interfacial tension measurements one of the most important considerations is the cleanliness of the vessels as well as the ring. All vessels must be chemically clean. The ring is cleaned by rinsing in naptha, rinsing in distilled water and flaming in the reducing flame of an ordinary burner. Flame only that portion of the ring which will be immersed in the liquid under test. To obtain repeat values the ring must be cleaned between each determination.

The calibration of any tensiometer should be checked periodically; especially each time the instrument is used after a period of idleness. In the following outline of operational procedure it is assumed that the instrument has been calibrated and is in adjustment.

a. <u>Surface Tension Measurement:</u>
To make a measurement of surface tension the cleaned ring is attached to the lever arm. The liquid to be measured is placed in a clean container such as an evaporating dish, watch glass or beaker at least 4.5 cm in diameter and the container placed on the sample, table. With screw (B) in its uppermost position raise the entire sample table assembly until the ring is immersed probably 5 mm in the liquid. Now lower the entire assembly until the ring is just below the 'surface of the liquid and approximately centered with respect to the container. Further lower the liquid by means of screw (B) until the ring is in the surface of the liquid and the index is approximately on zero.

Increase the torsion of the wire by rotating knob (A) and at the same time lower the sample table by means of screw (B) so as to keep the index on zero. The Index is to be kept on zero even though the surface of the liquid is distended. Continue this double movement until the film breaks.

The scale reading at the breaking point of the film is the apparent surface tension p.

b. <u>*Interfacial Tension Measurement:*</u>
Interfacial measurements that can be made with an upward pull may be made with either of these tensiometers. The accepted practice is to move the ring from water into the other liquid.

Ordinary adjustments are the same as for surface tension measurements. In raising or lowering the liquid make rough adjustments in height by moving the entire table assembly and fine adjustments by means of the screw (B).

When the measurement is to be made on the interface between water and a liquid lighter in density than water the ring pull is upward and the procedure is as follows. With water only in the clean dish, the platform is raised until the ring is immersed from 5 to 7 mm in the water. A quantity of the liquid is then carefully poured on the surface of the water. This should be to a depth of 5 to 10 mm depending upon the liquid but deep enough to prevent the ring from entering the upper surface before the film breaks. The position of the dish is adjusted until the ring is in the interface and the lever arm in the neutral position. Then the torsion of the wire is increased and the dish lowered, keeping the index of the lever arm at zero. The reading when the film at the interface breaks is the apparent interfacial tension p.

DETERMINATION OF APPARENT SURFACE AND INTERFACIAL TENSION

(Method: ASTM D971)

To make an interfacial measurement between water and liquid with density greater than water it is necessary to have an instrument which will exert a downward force on the ring. Cat. No. 70545 is the only tensiometer that can be used for this measurement. The procedure is as follows. The liquid of greater density is placed in the vessel to a depth of 10 mm or more, and then water to a depth of 5 mm poured on the surface of the liquid. The vessel is then raised until the ring is immersed in the water and is in the interface of the liquids with the lever arm index at zero. Increase the torsion on the wire to force the ring downward and simultaneously raise the vessel, keeping the lever arm index at zero. The scale reading when the film breaks is the apparent interfacial tension.

In all of the above measurements the scale reading on the instrument is the apparent surface or interfacial tension. According to Harkins and Jordan[1] and Freud and Freud[2] this value may differ from the true value by as much as 30% in extreme cases. For most measurements the difference is probably less than 5%. To obtain the true surface tension "/ it is necessary to correct the apparent surface tension p by a factor F so that

$$\gamma = p \times F$$

The reason for this correction and the method of obtaining the correction factor are outlined in the following section.

Since the surface tension is dependent upon temperature, the temperature at which the measurement is made should be noted. In most instances the measurements are made at 25°C.

3. CORRECTION FACTOR

Surface tension is a molecular property of liquids which produces a certain phenomena at their surface. It is a "skin effect" similar to a stretched membrane. Forces are tangential to the surface and are usually measured in dynes per centimeter. In case the surface tension separates two different liquids it is called interfacial tension.

In the case of surface tension measurements the ring is placed in the surface and the force necessary to withdraw it is measured. In this process of measuring, the ring is raised and the surface is distorted as shown in Fig. 5. As the upward movement of the ring continues, the distortion increases as shown in Fig. 6. Soon a rupture will occur where the two surfaces meet, and in this figure is marked "breaking point". Several things here will be noted. First, there are two surface films at each side which *introduces the figure 2 in the denominator of the equation Mg/2L. Next, it will be noted that the radius* from the center to the breaking point is less than the mean radius of the ring. Another feature is the clinging of a small amount of the liquid to the lower part of the ring. This latter effect, which accounts for the weight of the liquid clinging to the ring, is a function of the factors V, volume of liquid, and R, the radius of the ring. The former effect is affected by the ratio of the radius of the ring to the radius of the cross-section of the wire of the ring, i.e., R/r. These factors enter into the correction factor F, by which the apparent surface tension must be multiplied to give the true surface tension, γ.

Zuidema and Waters[3] have published a formula which accounts for these factors. To facilitate determining the correction factor, curves have been plotted with practical constants for these factors. Copies of these curves form a part of these directions.

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DETERMINATION OF APPARENT SURFACE AND INTERFACIAL TENSION

(Method: ASTM D971)

To use these curves it is necessary to know the ratio of the radius of the ring to the radius of the wire. The data R/r is furnished by the maker of the ring. It is also necessary to know the values of p, D, and d. In this case p is .the apparent surface tension, or reading on the tensiometer. When making a surface tension measurement, D is the density of the liquid, d is the density of saturated air. When making an interfacial measurement D is the density of the lower liquid, d the density of the upper liquid. In the case of surface tension, d, the density' of air, is so small in comparison to the density of most liquids that it may be ignored and the value of 1 used. Therefore, to determine the correction factor F, point off on the abscissa of the curve the value of p divided by the difference of (D-d), then refer this reading on the curve to the ordinate on the left which indicates the correction factor.

Maintenance. Extra torsion wires are supplied with each instrument. The wire as supplied is not calibrated. It is somewhat larger than necessary but experience has shown that individual calibration of the wire in the instrument in which it is used is necessary.

In replacing the torsion wire first remove the cover held in place by two screws. Tighten the screw (J) until the rear clamp spring support touches the post - this releases the tension in the wire. Remove the cap (R) and loosen the clamps at each end of the wire. Loosen the clamp securing the torsion arm to the wire. Handle the replacement wire carefully to avoid kinks. Secure the wire in the front clamp. Pull the wire fairly taut and secure it in the rear clamp. Release the screw (J) and the wire is held under the proper tension. Take care to see that the wire is not clamped in a twisted condition. Secure the torsion arm to the wire. When the torsion arm is clamped the torsion arm should be horizontal and the vernier should be in the lower left quarter of the dial (in a position corresponding to about seven on a clock).

After replacing the wire check the calibration of the instrument with weights as described previously in these directions. It will in general be found that the dial reading is less than the calculated value. To correct this the wire must be rubbed lightly with fine polishing paper to reduce the diameter. Exercise care in doing this and check the calibration frequently to avoid rubbing the wire more than required. When the calibration is approximately correct, final adjustment may be made by adjusting the length of the torsion arms as previously described.

References

1. Harkins and Jordan, Jour. Am. Chem. Soc., Vol. 52, p. 1751-72 (1930)
2. Freud and Freud, Jour. Am. Chem. Soc., Vol. 52, p.1772-82 (1930)
3. Zuidema and Waters, Ind. and Eng. Chem., Vol. 13, P.312, (1941)
4. ASTM Tentative Method D971-48T.

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TOTAL ORGANIC CARBON PROCEDURE

(Method: Walkley-Black$_1$)

Scope

The Walkley-Black method is a common acid digestion method for the analysis of organic matter in soils. The method in use since the 1930's uses chromic acid to measure the oxidizable organic carbon in the soil. The Walkley-Black method is very accurate and precise on soils with less than 2% organic matter. The Walkley-Black method may result in low-test results for soils with excessively high concentrations of organic matter due to the incomplete oxidation of organic carbon in the sample. The upper limit for the method is approximately 6% organic matter. The loss on ignition method should b used for soils containing >6% organic matter.

Method Summary

The Walkley-Black method involves a known volume of acidic dichromate solution reacting with an aliquot of soil in order to oxidize the organic carbon. The oxidation step is then followed by titration of the excess dichromate solution with ferrous sulfate. The organic carbon is calculated using the difference between the total volume of dichromate added and the volume titrated after reaction.

Laboratory Procedure

1. Obtain 15 grams of representative soil.
2. Extract samples by Dean-Stark method (if there is evidence of hydrocarbon) and dry for 16 hours in a vacuum drying oven at 150°F.
3. Grind soil using a mortar and pestle (no steel or iron) until it can pass through a #40 sieve (< 0.5 mm) making sure to clean the mortar and pestle between samples with methanol.
4. Weigh out 0.5-2 grams of soil: 0.5-1.5 grams for samples that appear to have organic material, 1-2 grams for clean samples. Record sample weight in TOC logbook along with ID, client, file number, date and flask number.
5. Transfer weighed material to a 500 ml Erlenmeyer flask.
6. Add 10 ml <u>EXACTLY</u> of fluid #1 (0.5N $K_2Cr_2O_7$) to each flask and agitate for 30 seconds making sure of complete mixing.
7. Add 20 ml <u>EXACTLY</u> of sulfuric acid, H_2SO_4, and increase the speed on the shaker to 2 on the speed setting. Agitate for one minute.
8. Set lab timer for 30 minutes and allow flasks to cool.
9. Add <u>EXACTLY</u> 200 ml of deionized water to each flask.
10. Remove flask from the shaker unit and add 3-4 drops of fluid #2 (Ferroin, o-Phenanthroline-ferrous complex 0.025M).
11. Drop a small clean stir bar into the flask. Place flask on stir plate and spin at low speed.
12. Record the starting volumetric reading for fluid #3 (0.5N Ferrous sulfate heptahydrate solution) burette in the TOC logbook. Always start the burette at the 25 ml mark or lower.
13. Slowly add fluid #3 until the mixture turns dark green, and then titrate drop by drop until the color changes <u>sharply</u> from blue to red.
14. Record the final burette reading in the TOC logbook.
15. Using the excel file TOC.xls, calculate the TOC value for each sample according to the following formula:

Organic Carbon, % = [[(meq K2Cr2O7 - meq FeSO4)(0.003)(100)]/soil weight, g] x response factor, rf.

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TOTAL ORGANIC CARBON PROCEDURE

(Method: Walkley-Black[1])

Reporting

Data is reported in tabular format and can be presented in an EDD format.

Quality Control

Blank Acceptance Range (RF): 97-103%, 1.261-133.9
Standard Acceptance Range: 70-130%
Method Detection Limit: 100 mg/kg (ppm)

(1) As listed in **METHODS OF SOIL ANALYSIS, Part 2, Chemical and Microbiological Properties, Second Edition:** American Society of Agronomy, Inc.; Soil Science Society of America, Inc. 1982

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PARTICLE SIZE BY DRY SIEVE PROCEDURE

(Method: ASTM D422-63 Reapproved 1998)

Scope

Particle size distribution of sediments is determined by sieving which consists of using a set of standard square-mesh, woven-wire cloth sieves that conform to ASTM E-11 in conjunction with a Ro-Tap mechanical shaker unit.

Weighed particles can range from 0.25 to 0.0012 inches and are determined as the fraction of each sample is collected and weighed in each standard sieve. The complete set of sieves is:

U.S. Sieve Number	Opening, Inches	Opening, mm	Phi of Screen
1	0.9844	25.002	-4.64
1/2	0.4922	12.501	-3.64
3/8	0.3740	9.500	-3.25
1/4	0.2500	6.351	-2.67
4	0.1873	4.757	-2.25
6	0.1324	3.364	-1.75
10	0.0787	2.000	-1.00
14	0.0557	1.414	-0.50
18	0.0394	1.000	0.00
25	0.0278	0.707	0.50
35	0.0197	0.500	1.00
40	0.0166	0.420	1.25
45	0.0139	0.354	1.50
60	0.0098	0.250	2.00
80	0.0070	0.177	2.50
120	0.0049	0.125	3.00
200	0.0029	0.074	3.75
270	0.0021	0.053	4.25
400	0.0015	0.037	4.75

Method Summary

The soil sample is dried and gently disaggregated using a wooden mortar and pestle. Samples that contain heavy concentrations of hydrocarbons are extracted by Dean-Stark distillation (API RP40) using either toluene or a chloroform-methanol azeotrope as the solvent prior to disaggregation. A representative portion of the sample, 50-1000 grams, is introduced into a stack of sieves beginning with U.S. Standard Sieve number 1/4 and is continuously shaken on the Ro-Tap shaker unit for a period of no less than 20 minutes and no greater than 30 minutes. Weights of the sample retained on each standard sieve number are recorded.

Quality Control

Calibration is determined by standards created by PTS Laboratories, Inc. by multiple size separation runs. Each screen is inspected prior to use for signs of excessive wear, distortion of the wire cloth or other aberrations. Sieves suspected of having a flaw are replaced and given to the laboratory supervisor for microscopic inspection, after which they are tested with standards, repaired or discarded. Duplicate samples are run for each batch of twenty samples and blind mixes of standards are run weekly. Duplicate sample acceptance ranges are 80-120 %, blind sample acceptance ranges are 90-110%.

PARTICLE SIZE BY DRY SIEVE PROCEDURE

(Method: ASTM D422-63 Reapproved 1998)

Reporting

Data is reported in tabular and graphical formats corresponding to the ASTM/USCS Classification system and can be presented in an EDD format. Statistical data of mean, median, standard deviation, sorting, skewness and kurtosis are included.

SAMPLE PREPARATION FOR PARTICLE SIZE ANALYSIS PROCEDURE

(ASTM D421/422M Method)

Sampling

1. Sub-sample approximately 20-30 grams of representative material at the requested interval.
2. Break up aggregations using a wood or rubber-covered pestle.
3. Dry sample at room temperature until weight is stable.
   a. If RUSH turnaround time is required, dry sample at 150°F until weight is stable.
   b. *If sample is contaminated with petroleum hydrocarbons, sample must be cleaned.*
      i. Package sample in thimble or cellulose envelope for Dean-Stark or Soxhlet extraction.
      ii. Extract for 4-8 hours or until sample is clean.
      iii. Dry sample at 150°F in vacuum oven until weight is stable.
4. For LPSA analysis, material passing a No. 10 (2.00-mm) sieve is required.
5. **Note:** For non-sediment (soil) samples, contact client to develop procedure.

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DRY OR NATIVE BULK DENSITY PROCEDURE

(Method: ASTM D2937-94)

Scope

This method covers the determination of in-place dry or native bulk density by the drive cylinder method. The method may also be modified for determining the dry bulk density of loose or "grab" samples by packing a cylinder.

Method Summary

Refer to Method ASTM D2937 for a detailed method summary.

Dry Density Procedure

1. Using calipers, determine the diameter and Length of the ring sample in centimeters. Calculate the bulk volume of the sample using the formula:

   Area = pi x r^2
   Length x Area = Bulk Volume in cubic centimeters

   Where r = sample radius (r = sample diameter/2)
2. Weigh sample in ring and dry in oven at 110°C for 24 hours or until weight stabilizes.
3. Weigh dry sample, remove soil from the ring and weigh empty ring.
4. Subtract ring weight from dry weight of sample and ring; divide result by the caliper measured bulk volume.
5. Report bulk density to the nearest 0.01 g/cc.

Native Density

1. Using calipers, determine the diameter and Length of the ring sample in centimeters. Calculate the bulk volume of the sample using the formula:

   Area = pi x r^2
   Length x Area = Bulk Volume in cubic centimeters

   Where r = sample radius (r = sample diameter/2)
2. Weigh samples in ring, remove soil from the ring and weigh empty ring.
3. Subtract ring weight from native weight of sample and ring; divide result by the caliper measured bulk volume.

Quality Control

Analyze one sample per batch using helium porosimetry or Archimedes method. Acceptance range is 90-110% of original value. Refer to Method ASTM D2937 for additional Quality control recommendations.

Reporting

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DETERMINATION OF TOTAL POROSITY PROCEDURE

(Method: API RP 40)

Scope

This method covers the determination total porosity by the Archimedes submersion method. Porosity is the ratio of the pore space to the bulk volume of the sample. Several other methods are available for measuring total porosity including mercury immersion and Boyle's Law. Refer to API RP 40 for full description.

Method Summary

Refer to the section on Porosity in API RP 40 for a detailed method summary.

Dry Density Procedure

1. Weigh dry plug sample to 0.01 gram.
2. Vacuum saturate the sample using toluene.
3. Weigh the toluene saturated plug sample to 0.01 gram.
4. Weigh the toluene saturated plug sample submerged in toluene to 0.01 gram.
5. Calculate the plug physical properties.
    a. Pore volume: (saturated weight – dry weight) / (density of saturant)
    b. Bulk volume: (saturated weight – immersed weight) / (density of saturant)
    c. Grain volume: (dry – immersed weight) / (density of immersion liquid)
    d. Porosity: (bulk volume – grain volume) / (bulk volume)

Quality Control

Blank Acceptance Range: 0.1 porosity units
Standard Acceptance Range is 98-102%.
Refer to the section on Porosity in API RP 40 for additional Quality Control recommendations.

Reporting

Data is reported in tabular format and can be presented in an EDD format

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